

Reactivity Ratios and Copolymer Composition Evolution During Styrene/Dimethacrylate Free-Radical Crosslinking Copolymerization

Walter F. Schroeder, Mirta I. Aranguren, Julio Borrajo

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata—National Research Council (CONICET), Argentina

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ABSTRACT: In this article, experimental and simulated results are presented for the evolution of the copolymer composition as unsaturations are consumed in the free-radical cross-linking copolymerization of Styrene(St) and BisphenolA glycerolate dimethacrylate (BDMA). Real time FTIR measurements were performed to monitor the depletion of each comonomer double bond during the isothermal curing reaction at 80°C. From the experimental data corresponding to different feed compositions, the initial reactivity ratios and their evolution with conversion were determined via a nonlinear least squares optimization of the integrated form of the copolymerization equation. The reactivity ratio of St increases continuously and exponentially with the overall reaction conversion, while that of BDMA decreases linearly. A modified terminal copolymer-

ization model including the dependence of the reactivity ratios with the overall conversion was proposed. The application of this model provides a consistent fitting for the conversion of each comonomer during all reaction stages, even at high conversion values where large diffusion and topological restrictions for chain movements are present. Simulations show that the concentration of styrene units added to the copolymer increases with the overall reaction conversion, while that for the BDMA double bonds diminishes. Structures rich in homopolymerized styrene are predicted at later stages of the reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3081–3091, 2010

Key words: dimethacrylate; copolymerization; reactivity ratios; radical polymerization; crosslinking

INTRODUCTION

Free-radical bulk copolymerization of a monounsaturated monomer with a polyunsaturated comonomer is one of the most efficient methods of synthesizing a highly crosslinked copolymer network.^{1,2} BDMA mixed with St as reactive diluent, constitutes one of the most important resin system of this category.³ Despite the increasing usage of BDMA resins, the relationships between their final properties and the polymerization conditions are not well understood because of the complexity of the chemistry, kinetics, and chemorheology of the crosslinking reaction. Therefore, a better understanding of the copolymerization process is desirable to design and control the structure and properties of the thermoset.

The curing reaction of a thermosetting system, such as St(1)/BDMA(2), can be described by the same steps of initiation, propagation and termination

as a linear free-radical copolymerization. At the propagation step, three types of possible bonds are formed in different proportions, 1-1, 2-2, and 1-2. At early stages of the reaction, polymerization changes from chemical to diffusion control, so the reaction rate depends primarily on the reactive species mobility. Initially, the change in the controlling mechanism manifests itself by an increase in the reaction rate due to diffusion controlled termination (gel effect). This initial self-acceleration effect is followed by a continuous reduction of the reaction rate due to the diffusion controlled propagation and to topological constraints produced by the poor accessibility of pendant reactive groups present in the sol macromolecules or in the gel structure.⁴⁻⁷ These effects are increasingly apparent throughout the cure reaction. Thus, at high conversions and in the case that the glass transition temperature of the reactive system reaches (or is near) the reaction temperature, the polymerization becomes diffusion controlled at all length scales, leading to a sharp decrease of the overall reaction rate.

To describe the radical copolymerization of a monounsaturated monomer with a polyunsaturated comonomer, the traditional approach for copolymerization^{4,8,9} can be used, since two different types of molecules having double bonds with different

Correspondence to: J. Borrajo (jborrajo@fi.mdp.edu.ar).

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reactivities must be considered. However, it must be additionally considered that the polyunsaturated comonomer has more than one reactive double bond. Diffusion control on the reaction rates can be taken into account by using an overall propagation rate constant that decreases with conversion^{10–12} and can be described by an empirical expression. By extension, the reactivity ratios, defined in the framework of the terminal copolymerization theory as the ratio of two propagation rates, should be conversion dependent too. Kinetic studies reported in the literature on St/BDMA systems^{13–16} show that the reactivity ratios are not constant throughout the crosslinking reaction. The reactivity ratio of the St increases during reaction, while that of the BDMA decreases. These changes are primarily produced by the different diffusive capabilities of the comonomers in the crosslinking medium.

In this work, an analysis of the free-radical crosslinking copolymerization of St and BDMA based on the terminal copolymerization theory, with the additional complexity of considering the variation of the reactivity ratios with the overall double bond conversion, is presented. This improved model takes into account, from a phenomenological point of view, the whole variety of diffusion and topological restrictions, including those associated to intramolecular cyclization reactions. Thus, it allows simulating the copolymerization behavior during the complete reaction process, even at high conversion values where strong diffusion and topological restrictions are present.

The Fourier transform infrared spectroscopy (FTIR) was the technique selected in this study to measure the depletion of double bonds of each monomer during the isothermal crosslinking copolymerization reaction. From the experimental data, the initial reactivity ratios and their evolution with the overall conversion were calculated. Then, the copolymerization model was applied and its predictions were compared with the experimental data. The model predicts copolymer structures which have been previously suggested in the literature.^{17–21}

THEORETICAL BACKGROUND

Copolymerization model

The model of free-radical crosslinking copolymerization of St and BDMA presented in this work is based on the Lewis-Mayo theory (terminal model)²² and is based on (relies on) three basic assumptions: (1) the terminal copolymerization theory is applicable with the reactivity ratios expressed as functions of the overall conversion of double bonds, (2) the two BDMA double bonds react independently, and (3) there are not concentration gradients due to microgel formation or gel heterogeneities.

To simulate the copolymerization reaction of St(M_1) and BDMA(M_2), the initial concentrations of M_1 and M_2 double bonds were expressed as molar fractions, $f_{1,0}$ and $f_{2,0}$ respectively; and a total initial number of double bond moles of $M_1 + M_2$, n_{0T} , was considered. The reaction was developed in successive steps to get the last overall conversion of double bonds, P_u . In each step k , Δn moles of M_1 and M_2 unsaturations are reacted and the formed copolymer has an instantaneous molar fraction $F_{1,k}$ of M_1 monomer.

In a particular step k , the molar fraction of M_1 units added to the copolymer is given by the copolymer equation^{23,24} of the form:

$$F_{1,k} = \frac{r_{1,k}f_{1,k}^2 + f_{1,k}f_{2,k}}{r_{1,k}f_{1,k}^2 + 2f_{1,k}f_{2,k} + r_{2,k}f_{1,k}^2} \quad (1)$$

where $f_{1,k}$ and $f_{2,k}$ are the unsaturation molar fractions of M_1 and M_2 in the feed at the particular step k ; while that $r_{1,k}$ and $r_{2,k}$ are the reactivity ratios during the same step. Since the number of global double bond moles reacted up to the k step is known, the overall conversion can be calculated as:

$$P_k = \frac{k\Delta n}{n_{0T}} \quad (2)$$

A mass balance of M_1 unsaturations between the steps ($k-1$) and k , is used in the simulations to obtain the molar fraction of M_1 unsaturations in the feed at the k step ($f_{1,k}$), as follows:

$$(n_{0T} - k\Delta n)f_{1,k} + F_{1,k}\Delta n = [n_{0T} - (k-1)\Delta n]f_{1,(k-1)} \quad (3)$$

The increment of the M_1 and M_2 double bond conversion in the k step can be calculated from the number of moles of M_1 or M_2 double bonds added to the copolymer in this step, in the following way:

$$\Delta P_{1,k} = \frac{F_{1,k}\Delta n}{n_{0T}f_{1,0}} \quad \Delta P_{2,k} = \frac{(1 - F_{1,k})\Delta n}{n_{0T}(1 - f_{1,0})} \quad (4)$$

The M_1 and M_2 double bond conversions after k reaction steps are calculated from the sum of the accumulated increments during all the previous steps, as:

$$P_{1,k} = \sum_{i=1}^k \Delta P_{1,i} \quad P_{2,k} = \sum_{i=1}^k \Delta P_{2,i} \quad (5)$$

These monomer double bond conversions, $P_{1,k}$ and $P_{2,k}$, and the overall conversion up to the k step, P_k , are related by the following equation:

$$P_k = P_{1,k}f_{1,0} + P_{2,k}(1 - f_{1,0}) \quad (6)$$

The reactivity ratios, r_1 and r_2 , are defined in the copolymerization model as the ratios of the two propagation rate constants k_{11}/k_{12} and k_{22}/k_{21} , respectively. These rate constants are average values of the propagation reactions that take place at a given conversion. The reactions between free radicals and double bonds occurring in each propagation step are affected by a wide distribution of diffusion and topological restrictions (DTR). This variety of restrictions are originated in the fact that the reactive species (radicals and unsaturations) can form part of the soluble fraction of the copolymer, belonging to molecules with a wide distribution of sizes and chemical structures, or they can form part of the gel fraction, belonging to pendant chains inside the macrogel network with different local environments and mobilities. As a consequence, the rate constants and the reactivity ratios depend on the intrinsic chemical reactivity of the radicals and unsaturations, their concentration, accessibility, as well as the mobility of the molecules and structures to which they are bonded.

If one of the double bonds of M_2 has reacted, the reactivity of the remaining unsaturation can be markedly impaired depending on the different degrees of restrictions imposed on its mobility and availability when it is attached to a sol molecule or to a pendant chain bonded to the macrogel. It is expected that at increasing conversions, the reactivity ratio $r_1 = k_{11}/k_{12}$ will increase continuously because the availability of M_1 radicals to react with M_2 double bonds decreases drastically in comparison to that with the M_1 unsaturations. For the same reason, the reactivity ratio $r_2 = k_{22}/k_{21}$ decreases continuously with the increasing global conversion. Studies carried out on the St-BDMA copolymerization kinetics¹³⁻¹⁵ have shown that the reactivity ratio of the St increases, and simultaneously that of the BDMA decreases, during crosslinking reaction. To simulate the experimental behavior, the following empirical functions of the reactivity ratios with the overall conversion are proposed:

$$r_{1,k} = \frac{k_{11,k}}{k_{12,k}} = \frac{k_{11,0}}{k_{12,0}} f(P_k) = r_{1,0} \left(1 - \frac{P_k}{P_u}\right)^R \quad (7)$$

$$r_{2,k} = \frac{k_{22,k}}{k_{21,k}} = \frac{k_{22,0}}{k_{21,0}} g(P_k) = r_{2,0} \left(1 - \frac{P_k}{P_u}\right)^S \quad (8)$$

where $k_{11,k}$, $k_{12,k}$, $k_{22,k}$, and $k_{21,k}$ are the propagation rate constants in the k step; $k_{11,0}$, $k_{12,0}$, $k_{22,0}$, and $k_{21,0}$ are the propagation rate constants at zero conversion; $r_{1,0}$ and $r_{2,0}$ are the isothermal reactivity ratios of M_1 and M_2 at zero conversion; P_k and P_u are the

overall double bond conversions in the k step and at the end of the reaction, respectively; and R and S are the only empirical fitting parameters. Similar approaches to take into account the diffusion and topological restrictions on the propagation rate constants in styrene-unsaturated polyester systems have been proposed by other researchers.^{11,25}

The number average sequence lengths of M_1 and M_2 unsaturations added to the copolymer in the k step, $\bar{n}_{1,k}$ and $\bar{n}_{2,k}$, are given by the following equations:

$$\bar{n}_{1,k} = 1 + r_{1,k} \frac{f_{1,k}}{f_{2,k}} \quad \bar{n}_{2,k} = 1 + r_{2,k} \frac{f_{2,k}}{f_{1,k}} \quad (9)$$

For the simulation runs, the n_{0T} and Δn parameters were fixed in 10,000 moles and 1 mol, respectively. The initial reactivity ratios, $r_{1,0}$ and $r_{2,0}$, were calculated from experimental data acquired at the early reaction stages. The final overall conversion, P_u , was determined from the particular double bond conversions at the end of each reaction; and the R and S parameters were also estimated from the experimental data, as it will be discussed in "Evolution of the reactivity ratios" section.

Determination of the reactivity ratios

The reactivity ratios can be evaluated by using the integrated form of the copolymerization equation [eq. (10)], where P is the overall double bond conversion, $f_{1,0}$ and $f_{2,0}$ are the initial molar fractions of St and BDMA double bonds in the feed, and f_1 and f_2 are the actual molar fractions of double bonds of each one in the feed at conversion P ,²⁴

$$(1 - P) = \left(\frac{f_1}{f_{1,0}}\right)^\alpha \left(\frac{f_2}{f_{2,0}}\right)^\beta \left(\frac{f_{1,0} - \delta}{f_1 - \delta}\right)^\gamma \quad (10)$$

where $\alpha = \frac{r_2}{1 - r_2}$, $\beta = \frac{r_1}{1 - r_1}$, $\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$, $\delta = \frac{1 - r_2}{2 - r_1 - r_2}$

This method requires to fit the experimental conversion data to eq. (10) and to obtain r_1 and r_2 values as the best fitting parameters from a nonlinear least squares optimization.

Azeotropic copolymerization

If the copolymerization is carried out under azeotropic conditions, the composition of the copolymer being formed equals that of the feed mixture, hence copolymerization proceeds without concentration changes in the comonomer feed mixture and copolymer composition. In the framework of the terminal copolymerization theory, the azeotropic composition is given by the following equation:^{23,24}

TABLE I
Chemical Structure of the Comonomers

Name	Chemical structure
BisphenolA glycerolate dimethacrylate (BDMA)	
Styrene (St)	

$$(f_1)_{az} = \frac{1 - r_2}{2 - r_1 - r_2} \quad (11)$$

Thus, azeotropic copolymerizations can only occur when both reactivity ratios are either smaller than or greater than unity.

EXPERIMENTAL

Materials and sample preparation

BisphenolA glycerolate dimethacrylate (BDMA) (Esstech, Essington, PA) and St (Poliresinas San Luis S.A., San Luis, Argentina) were used as received. Table I shows the chemical structure of these two reactants. The molar mass of BDMA determined by size exclusion chromatography (SEC) (Waters Model 440, Waters, Milford, MA) using columns PLGel (Torrance, CA) of 100, 500, 10³, 10⁴, and 10⁶ Å in distilled tetrahydrofuran (Laboratorios Cicarelli, Argentina; analytical reagent) was 600 g/mol, using polystyrene calibration. Benzoyl peroxide (Luzidol 75%, Akzo Chemicals S.A., Buenos Aires, Argentina) was the initiator of the free-radical polymerization and was used as received.

The BDMA was diluted with different proportions of styrene in the range of 15 to 55 wt % ($f_{0,St}$ between 0.38 and 0.81). Initially, the BDMA was dissolved in St at 40°C, and then the mixture was allowed to cool down to room temperature. After that, 2 wt % of benzoyl peroxide was added and dissolved in the mixture.

FTIR measurements

Monitoring of the curing reactions was performed using a Genesis II Mattson FTIR (Mattson, Madison, WI) spectrometer in the transmission mode. A drop of the sample was sandwiched between two KBr crystal discs separated by a 50 µm aluminum spacer ring used to regulate the sample thickness and to avoid evaporation of styrene. The assembly was placed in a sample oven HT-32 (Spectra-Tech, Shelton, CT) with programmable temperature control, which was then mounted into the spectrometer. The sample temperature was maintained to within 80 ± 0.5°C and FTIR measurements were taken in real

time. FTIR spectra were acquired in absorbance mode over the range of 600–2000 cm⁻¹ from eight coadded scans at 2 cm⁻¹ resolution. The acquisition was carried out until no changes in the absorbance peak area were observed. The conversion profiles were calculated from the decay of the absorption bands located at 910 cm⁻¹ (vinyl group of the St) and at 945 cm⁻¹ (vinyl groups of the BDMA) as described by Brill and Palmese.¹⁷ The absorption intensities assigned to bending of aromatic carbon–hydrogen bonds at 830 cm⁻¹ in BDMA and at 700 cm⁻¹ in St were used to correct for any changes in sample thickness during polymerization. By calling $A(t)$ to the absorption intensity of the peaks at time t , the fractional conversions of double bonds of St (P_1) and BDMA (P_2) are defined by:

$$P_1(t) = 1 - \left(\frac{A_{910}(t)}{A_{910}(t=0)} \right) \left(\frac{A_{700}(t=0)}{A_{700}(t)} \right) \quad (12)$$

$$P_2(t) = 1 - \left(\frac{A_{945}(t)}{A_{945}(t=0)} \right) \left(\frac{A_{830}(t=0)}{A_{830}(t)} \right) \quad (13)$$

while the overall double bond conversion at time t is calculated as:

$$P(t) = f_{1,0}P_1(t) + f_{2,0}P_2(t) \quad (14)$$

where $f_{1,0}$ and $f_{2,0}$ are the initial molar fractions of double bonds of St and BDMA comonomers, respectively.

RESULTS AND DISCUSSION

Measurements of double bond conversion

The FTIR measurements taken in real time were performed to monitor the St and BDMA double bond conversion during their free-radical crosslinking copolymerization in samples with initial feed concentrations in the range of 15–55 wt % St (corresponding to $f_{0,St}$ between 0.38 and 0.81) and cured isothermally at 80°C. Figure 1 shows transmission spectra acquired at different times during cure of the sample containing 25 wt % St ($f_{0,St} = 0.54$). The decay of the absorption peaks located at 945 and 910 cm⁻¹, assigned to out-of-plane bending of

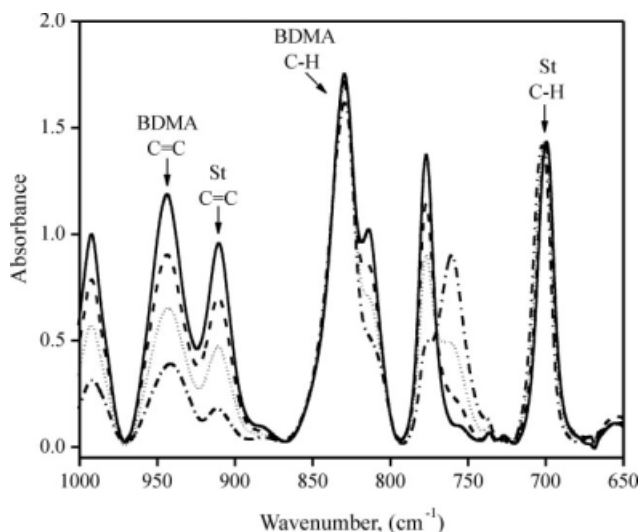


Figure 1 Representative FTIR spectra acquired at different times during the curing (at 80°C) of a St-BDMA sample containing 25 wt % St ($f_{0,St} = 0.54$): (—) 0 min; (---) 33 min; (····) 36 min; (- · - ·) 120 min. Only the region used for the calculations is shown.

carbon-hydrogen bonds in the vinyl group of the BDMA and the wagging of CH_2 in the vinyl group of the St, respectively, were monitored independently to calculate the conversion of St and BDMA double bonds during copolymerization. It should be pointed out that the FTIR technique would lead to an underestimation of the final conversion of BDMA double bonds by about 5%, as evaluated in Ref. ¹⁷. Figure 2 shows the double bond fractional conversion of each comonomer as a function of time. It can be seen that for this particular composition, the initial conversion rates are almost the same. This feature is related with the fact that this composition presents an initial azeo-

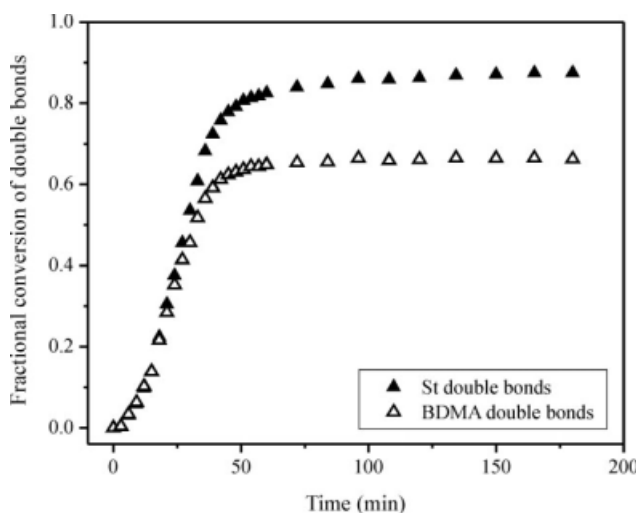


Figure 2 Fractional conversion of St and BDMA double bonds as a function of time, for the 25 wt % St mixture ($f_{0,St} = 0.54$) cured isothermally at 80°C.

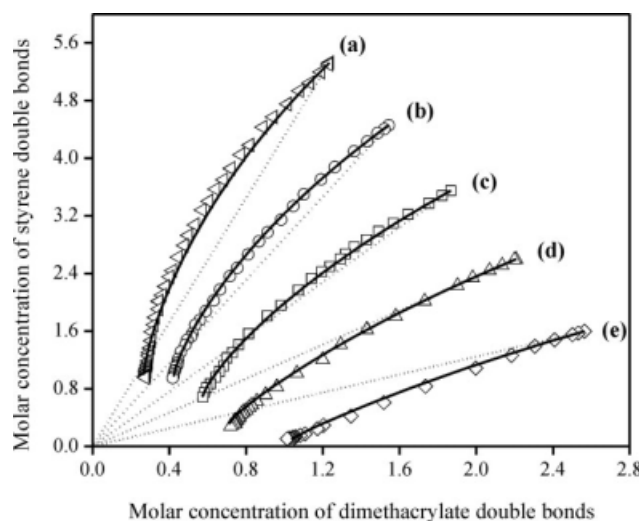


Figure 3 Evolution of St and BDMA double bond molar concentration in the feed for different initial comonomer mixtures: (a) 55 wt % St ($f_{0,St} = 0.81$), (b) 45 wt % St ($f_{0,St} = 0.74$), (c) 35 wt % St ($f_{0,St} = 0.66$), (d) 25 wt % St ($f_{0,St} = 0.54$), (e) 15 wt % St ($f_{0,St} = 0.38$). Symbols represent experimental data; (—) model predictions; and (····) expected azeotropic behavior without DTR effects.

tropic behavior, as it will be later proved. It is also observed, that the reaction of St continues after the reaction of BDMA was severely arrested. This behavior will be discussed in the following sections in light of the analysis of the experimental data.

Figure 3 shows the experimental data for the depletion of the molar concentration of double bonds of each comonomer in the feed during copolymerization of the different mixtures tested. These values were calculated from the conversion data of the comonomers and the initial molar concentration for each mixture. The final double bond conversions reached by St and BDMA, as well as the final overall conversion for each formulation analyzed are listed in Table II.

Estimation of the model parameters

Initial reactivity ratios

The initial St and BDMA reactivity ratios were calculated from the experimental data obtained at early

TABLE II
Final Double Bond Conversions Reached by St (P_{1u}) and BDMA (P_{2u}), and Final Overall Conversion (P_u), for the Different Feed Compositions Studied

Initial feed composition				
wt % St	$f_{0,St}$	P_{1u}	P_{2u}	P_u
15	0.38	0.93	0.60	0.73
25	0.54	0.89	0.67	0.79
35	0.66	0.81	0.69	0.77
45	0.74	0.79	0.73	0.77
55	0.81	0.82	0.78	0.81

conversions (<8%), where diffusion and topological restrictions do not significantly affect the behavior of the reactive species.²⁶ From the variation in double bond concentrations, the reactivity ratios were determined by using the integrated form of the copolymerization equation [eq. (10)]. For this purpose, the methodology proposed by Aguilar and co-workers²⁷ was employed. Feed composition values (f_1 , f_2) obtained in the range of overall conversions (P) between 0 and 0.08 were fitted to eq. (10) and a nonlinear least squares optimization led to the best values of r_1 and r_2 . During analysis, the reactivity ratios were used as the only fitting parameters to satisfy the least squares condition, $\min \sum [(1 - P)_{\text{calculated}} - (1 - P)_{\text{exp}}]^2$, for the experimental data acquired at this early reaction stage for all the tested initial feed compositions. The best set of these two parameters that could fit all experimental data was obtained using the Levenberg-Marquardt algorithm. Standard deviations of the optimized parameters were estimated on the basis of the theory of error propagation.^{28,29} The following set was obtained: $r_{1,0} = 0.43 \pm 0.03$ (for styrene); and $r_{2,0} = 0.41 \pm 0.05$ (for BDMA), which are in good agreement with previously reported values.³⁰

These values indicate that each free-radical prefers to add to one double bond of the other comonomer at the beginning of the reaction. To model the compositional changes in the feed and the copolymer with the increasing overall conversion, the changes of the reactivity ratios as the copolymerization proceeds must be considered. These changes have to be followed up to the point at which the reaction is stopped because the system becomes glassy at the selected reaction temperature.

Evolution of the reactivity ratios

As the overall degree of polymerization increases, the reactivity of the long BDMA chains became limited because of their reduced mobility, while the smaller and more mobile St molecules can still diffuse and react through the restricted medium. It should be also considered that when one of the double bonds in the BDMA has reacted, the reactivity of the remaining one can be markedly reduced due to the lower mobility of the structure to which it is connected. The effect of a rapid build-up of a 3D network structure with increasing number of reactive pendant double bonds and radicals leads to a diffusion and topological control on fundamental reaction steps. In this way, the rate constants and by extension, the reactivity ratios become dependent on the whole conversion P . As a consequence, it is expected that the reactivity ratio of the St increases and simultaneously that for BDMA decreases during the cross-linking reaction, and that these changes in the reac-

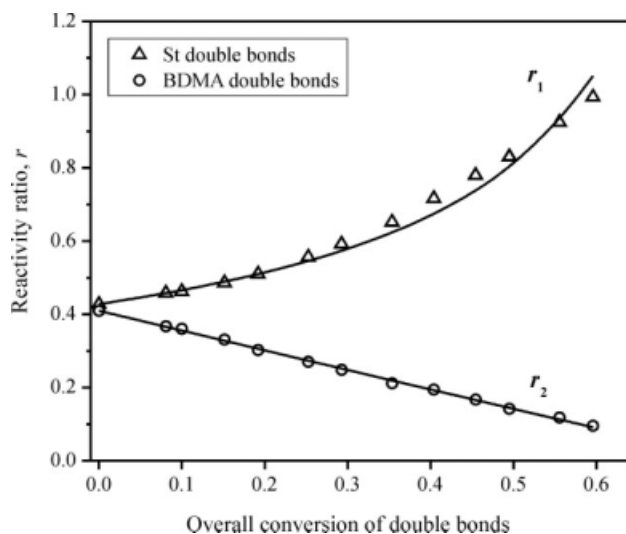


Figure 4 Evolution of St and BDMA reactivity ratios during copolymerization of the mixture with 45 wt % St ($f_{0,\text{St}} = 0.74$). Symbols represent values obtained from the experimental data; and (—) values calculated from eqs. (7) and (8) using the calculated R and S parameters.

tivity ratios can be expressed as functions of the overall conversion.

To analyze the variation of the reactivity ratios during the copolymerization reaction, a method of parameter estimation by nonlinear least squares optimization similar to that used to determine the initial reactivity ratios was used. A polynomial fitting equation for f_1 and f_2 as a function of the global conversion P was computed from the experimental data for St and BDMA double bond consumption. Using this expression, it was possible to obtain by interpolation multiple data sets, with 40 points (f_1 , f_2), that correspond to overall conversion advances of 1%. Then, each data set was fitted to eq. (10) using the Levenberg-Marquardt algorithm and obtaining the reactivity ratios, $r_{1,k}$ and $r_{2,k}$, as the only fitting parameters for each particular data set. Reactivity ratio values obtained for each analyzed data set were assigned to the average overall conversion of the set. In this way, the evolution profile of the reactivity ratios with overall conversion was obtained for each initial feed concentration during the copolymerization reaction. Figure 4 shows the obtained results for the mixture with 45 wt % St ($f_{0,\text{St}} = 0.74$). As expected, the reactivity ratio of the St (r_1) increases with conversion and simultaneously that of the BDMA (r_2) decreases. It can also be observed that r_1 increases at a growing rate during the whole reaction, while r_2 decreases at a constant rate. Similar trends were obtained for the other feed concentrations analyzed.

From the obtained values of the reactivity ratios as functions of the overall conversion, the parameters R and S , in eqs. (7) and (8), were estimated. It is

TABLE III
Optimized Values for the Parameters R and S , in eqs. (7) and (8), for the Different Feed Compositions Studied

Initial feed composition			
wt % St	$f_{0,St}$	R	S
15	0.38	-0.60	1.17
25	0.54	-0.63	1.06
35	0.66	-0.62	1.03
45	0.74	-0.62	1.03
55	0.81	-0.58	1.01

important to emphasize that these equations are proposed in the model to represent the effect of the diffusion and topological restrictions (DTR) on the reactivity ratios during simulations. Nonlinear least squares analyzes were performed by fitting the values obtained for the St to eq. (7) using R as the only fitting parameter, and those obtained for the BDMA to eq. (8) using in this case S as the fitting parameter. The initial reactivity ratios estimated in the previous section, and the final overall conversion measured for each reaction (Table II), were used during calculations. Table III shows the values of R and S obtained for each feed concentration analyzed. In all cases, the error in the estimation of these parameters was always below ± 0.02 . It can be observed that no significant changes in the R and S values were obtained in the composition range studied. As it will be discussed in "Conversion of St and BDMA" section, this feature allows simulating all the tested feed compositions using only one set of values for the R and S parameters. Figure 4 shows the reactivity ratios calculated with eqs. (7) and (8), using the values of R and S obtained for the feed mixture with 45 wt % St ($f_{0,St} = 0.74$). As it can be seen, the proposed functions fit very well the behavior of the reactivity ratios during the crosslinking reaction. In fact, excellent fitting were obtained for all the analyzed feed concentrations, using the values for R and S listed in Table III.

Model predictions

Azeotropic behavior

In the framework of the terminal copolymerization theory, the azeotropic composition is given by eq. (11). Using the obtained values for the initial reactivity ratios of St ($r_{1,0} = 0.43$) and BDMA ($r_{2,0} = 0.41$) in that equation, the initial azeotropic concentration for the system is: $(f_1)_{az} = 0.51$ (which corresponds to 23 wt % of St).

From eq. (11), it can be obtained the relationship between the values of r_1 and r_2 that keeps the concentration of the feed and the copolymer constant and equal to the initial value of $(f_1)_{az} = 0.51$. This

relationship is given by: $r_1 = 0.04 + 0.96 r_2$. This equation could be satisfied if the instantaneous r_1 and r_2 pairs are simultaneously increasing or decreasing in the whole conversion range. But this requirement is in contradiction with the variations observed in the reactivity ratios during the copolymerization (Fig. 4), in which r_1 increases but r_2 decreases during reaction due to the DTR effects.

Because of the variations produced in the values of r_1 and r_2 , the composition that satisfies the azeotropic behavior, $F_1 = f_1$, will increase during the whole reaction. The predictions of the changes in the azeotropic concentration for the different initial feed concentrations are shown in Figure 5. The horizontal line corresponds to the initial azeotropic mixture [$(f_1)_{az} = 0.51$] without taking into account DTR effects during the reaction, and represents the "classical azeotropic" behavior in the sense of the Lewis-Mayo copolymerization theory. Since the initial reactivity ratios are the same in all the studied feed mixtures, it can be observed that all these mixtures present the same azeotropic behavior at zero conversion. It is interesting to appreciate that differences between the real and classical azeotropic behaviors become more pronounced with increasing concentration of BDMA (crosslinker) in the feed mixture. This occurs because for the same global conversion, the feed mixtures presenting higher crosslinking densities also show more intense DTR effects.

This analysis shows that it is impossible to find a "classical azeotropic" behavior during cure of St-BDMA mixtures; even the formulation with 25 wt %

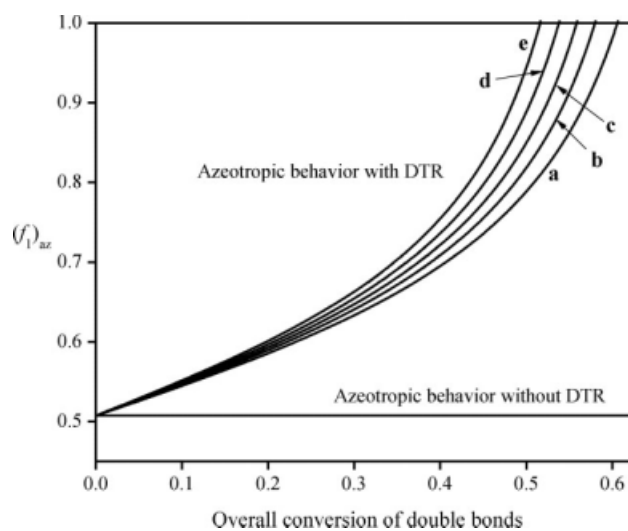


Figure 5 Calculated evolution of the azeotropic concentration against the overall double bond conversion for different initial St concentrations: (a) 55 wt % St ($f_{0,St} = 0.81$), (b) 45 wt % St ($f_{0,St} = 0.74$), (c) 35 wt % St ($f_{0,St} = 0.66$), (d) 25 wt % St ($f_{0,St} = 0.54$), (e) 15 wt % St ($f_{0,St} = 0.38$). The "classical azeotropic" behavior (not affected by DTR effects) of a mixture with the initial azeotropic concentration ($f_{0,St} = 0.51$) is included for comparison.

St ($f_{0,St} = 0.54$), which is very near the initial azeotropic concentration, shows the typical up-bending behavior also observed in other radical crosslinking systems formulated with polyunsaturated comonomers, typically in St-unsaturated polyester (UP) systems.

Conversion of St and BDMA

The predictive capabilities of the proposed model were demonstrated by using it to simulate the particular consumption of double bonds throughout the reaction. As it was previously mentioned, Table III shows that the parameters R and S , in eqs. (7) and (8), do not vary significantly with the initial feed concentration in the range studied. This result indicates that it should be possible to model all the studied mixtures using only one pair values for R and S . In fact, when the model was applied using the average R and S values for all the compositions, the predicted copolymerization features were essentially the same as those obtained with the R and S values calculated for each different initial feed. This is an interesting characteristic of the system because it allows analyzing the behavior of any mixture in this composition range using the same R and S parameters. Thus, in the rest of the study all the simulations were carried out using the set of average values: $R = -0.61$ and $S = 1.06$.

Figure 3 shows simulated results for the depletion of the molar concentration of double bonds of each comonomer in the feed during copolymerization of the different mixtures tested. An excellent fit of the experimental data points was obtained for all the studied compositions. The dotted lines in the plot indicate, for each initial concentration sample, the expected compositional drift if the system would react following an azeotropic behavior. It can be seen that the mixture with 25 wt % St ($f_{0,St} = 0.54$) shows an initial behavior very close to the azeotropic one, in agreement with the classical azeotropic composition calculated in the previous section [$(f_1)_{az} = 0.51$]. As the copolymerization progresses, an increasing deviation from this behavior is observed due to the preferential incorporation of St to any radical present in the growing crosslinked copolymer, in comparison with BDMA. This effect is originated by the higher mobility of the St molecules inside the swollen network. Consequently, there is a higher availability of St double bonds than that of BDMA double bonds; the addition of the last ones being severely affected by the DTR. At the end of the reaction, St reacts almost exclusively originating very long sequences of St units in the crosslinked copolymer.

In Figure 3, it can be seen that the curves corresponding to mixtures with 35, 45, and 55 wt % St

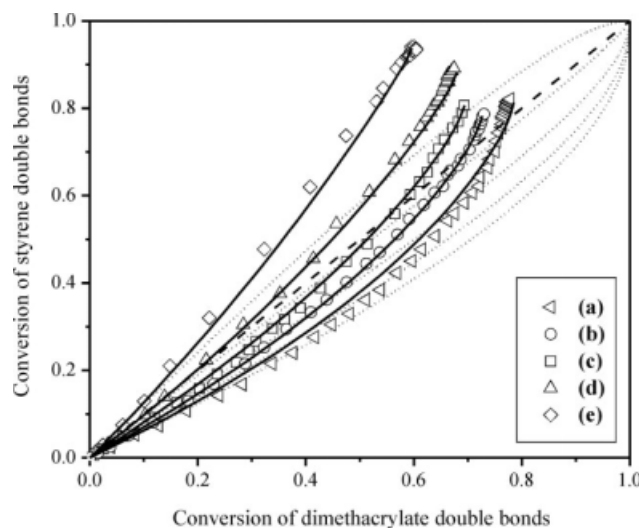


Figure 6 Evolution of St double bond conversion against BDMA double bond conversion for the different mixtures tested: (a) 55 wt % St ($f_{0,St} = 0.81$), (b) 45 wt % St ($f_{0,St} = 0.74$), (c) 35 wt % St ($f_{0,St} = 0.66$), (d) 25 wt % St ($f_{0,St} = 0.54$), (e) 15 wt % St ($f_{0,St} = 0.38$), (—) model predictions; (····) expected behaviors without DTR effects; (- - -) “classic azeotropic” behavior for a mixture with 23 wt % St ($f_{0,St} = 0.51$) without DTR effects.

($f_{0,St}$ equal to 0.66, 0.74, and 0.81 respectively) start above the azeotropic line. This fact indicates that for these compositions, at early stages of conversion, the double bonds of BDMA react at a higher ratio than the St ones. However, as conversion increases the BDMA double bonds become less reactive than those of St because of DTR effects, so the curves intersect the azeotropic line. At the later stages of the reactions, mostly St incorporates into the St-BDMA copolymer. On the other hand, in the mixture with 15 wt % St ($f_{0,St} = 0.38$) the styrene reacts at a higher ratio during the whole reaction. These results indicate that the initial composition of the feed mixture significantly affects the developed network structure.

Complementary information is illustrated in Figure 6, which shows the results in the form of St double bond conversion plotted against the BDMA double bond conversion. This type of plot shows a typical up-bending behavior, which has been frequently observed during the copolymerization of styrene-unsaturated polyester (St-UP) systems^{31–33} and is presented here to emphasize the similarity of the behaviors of both St-UP and St-BDMA reactive systems. The diagonal dashed line represents the classic azeotropic behavior without DTR effects ($P_1 = P_2$). As it has been also observed in St-UP systems, for all mixtures with initial styrene concentration higher than the azeotropic one [$(f_1)_{az} = 0.51$] the curves begin below the diagonal, because initially $P_2 > P_1$, as it was previously discussed. As the degree of polymerization increases, the curves

intersect the $P_1 = P_2$ line showing the characteristic up-bending behavior caused by effects of DTR on the reactivity ratios. On the contrary, for the system with 15 wt % St ($f_{0,St} = 0.38$) the curve begins above the diagonal line (because $P_1 > P_2$) and increases monotonously.

The constant reactivity predictions (dotted lines in Fig. 6) were calculated taking $R = S = 0$ in eqs. (7) and (8). It can be seen that at low conversions all mixtures present the classical behavior and experimental points fall on the model predictions without DTR effects, since these are negligible at very low conversions (P_1 and $P_2 < 0.15$). However, as the degree of polymerization increases significant deviations towards higher styrene conversions are produced due to the effects of the DTR on the reactivity ratios.

Finally, it is possible to argue from the previous results that the R and S parameters are physically related to the mobility of the species containing reactive unsaturations and its influence on the propagation constants. From eq. (7), it can be noticed that although both propagation constants (k_{11} and k_{12}) decrease with the increasing global conversion as a consequence of diffusion and topological effects, k_{12} should be more affected than k_{11} because of the lower mobility of the species containing M_2 unsaturations (BDMA in the sol or gel phases) with respect to those species with M_1 unsaturations (St in the soluble phase). As a consequence, the k_{11}/k_{12} ratio increases with the conversion conducting to a negative exponent ($R = -0.61$) in the eq. (7). A similar argument can be used for the analysis of S in eq. (8). Both k_{22} and k_{21} decrease with conversion, but from the same argument given above, the k_{22}/k_{21} ratio decreases with conversion leading to a positive exponent ($S = 1.06$).

Copolymer composition

The model predictions for the instantaneous concentration of St and BDMA double bonds added to the copolymer (F_1 , F_2) throughout the reaction are shown in Figure 7. For all the studied mixtures the concentration of St units added to the crosslinking copolymer increases during the entire reaction. This behavior is due to the continuous increase of the St reactivity ratio, and the consequent decrease of the BDMA one, during the reaction. At later stages, the instantaneous concentration of St in the copolymer noticeably increases in agreement with the results shown in Figures 3 and 6.

As it was discussed in the previous section, in the sample with initial concentration of 15 wt % St (corresponding to $f_{0,St} = 0.38$) $P_1 > P_2$ at all conversions (Fig. 6). However, Figure 7 shows that for the same mixture and at global conversions below 0.4, the molar fraction of BDMA double bonds added to the

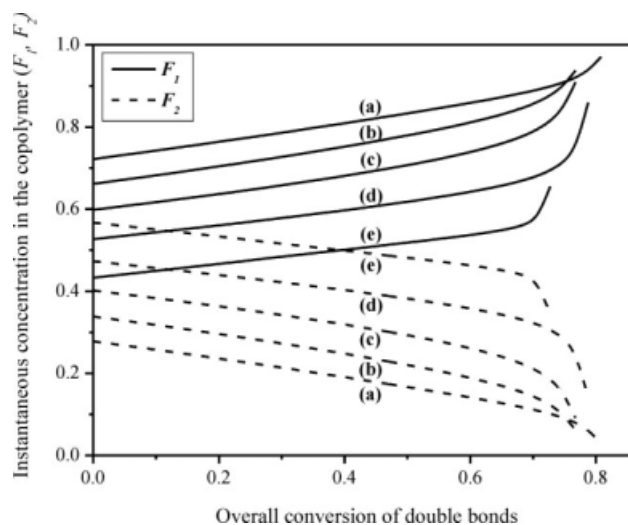


Figure 7 Instantaneous concentration in the copolymer (F_1 , F_2) as a function of overall double bond conversion for different initial feed concentrations: (a) 55 wt % St ($f_{0,St} = 0.81$), (b) 45 wt % St ($f_{0,St} = 0.74$), (c) 35 wt % St ($f_{0,St} = 0.66$), (d) 25 wt % St ($f_{0,St} = 0.54$), (e) 15 wt % St ($f_{0,St} = 0.38$).

copolymer is higher than that of the St. This behavior appears because the effect of the increase of the St reactivity ratio (caused by the DTR) is surpassed by the effect of the higher than the azeotropic concentration of BDMA double bonds in the feed. For conversions above the crossing point ($P = 0.4$), the F_1 and F_2 curves diverge due to the DTR effect.

For an initial St concentration of 23 wt % (azeotropic mixture, not shown in Fig. 7) the cross-over of the curves for St and BDMA would be located at zero conversion, $P = 0$, with $(F_1)_{az} = (f_1)_{az} = 0.51$, the azeotropic concentration. For all the other mixtures with initial St concentration higher than the azeotropic one, $F_1 > F_2$ from $P = 0$. All these curves diverge from the start of the copolymerization reaction due to DTR effects.

The analysis of the results for the sample with 15 wt % St ($f_{0,St} = 0.38$) in Figures 6 and 7 shows that a higher conversion value for St double bonds does not necessarily mean that a higher number of St double bonds have been added to the copolymer. This is also true for all samples with initial St concentration lower than the azeotropic one [$(f_1)_{az} = 0.51$]. An opposite behavior is observed for the samples with 25, 35, 45, and 55 wt % St (corresponding to $f_{0,St}$ equal to 0.54, 0.66, 0.74, and 0.81 respectively), for which initially $P_2 > P_1$ and the concentration of St double bonds added to the copolymer is higher than that of BDMA during the whole copolymerization reaction.

The Figure 8 shows the model predictions for the instantaneous number average sequence lengths of double bonds of St (1-1) and BDMA (2-2) added to

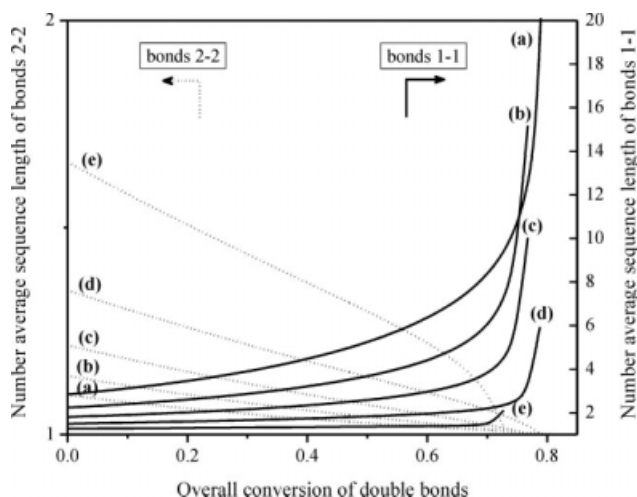


Figure 8 Instantaneous number average sequence lengths of St (1-1) and BDMA (2-2) double bonds added to the copolymer as a function of the overall double bond conversion, for different initial feed concentrations: (a) 55 wt % St ($f_{0,St} = 0.81$), (b) 45 wt % St ($f_{0,St} = 0.74$), (c) 35 wt % St ($f_{0,St} = 0.66$), (d) 25 wt % St ($f_{0,St} = 0.54$), (e) 15 wt % St ($f_{0,St} = 0.38$).

the copolymer, as a function of the overall conversion. It can be seen, that at any conversion value, the sequence of (1-1) bonds is longer for higher initial concentrations of St. This is due to the higher number of St double bonds available in the feed. For all studied mixtures, the sequence length of (1-1) bonds increases throughout the reaction as a consequence of the increase of the St reactivity ratio with the overall conversion due to DTR. On the other hand, the mixture with higher content of BDMA [Fig. 8(e)] presents an initial average length of (2-2) sequences shorter than 2 units, which decreases down to the final value of 1 as reaction proceeds. In fact, for all the studied mixtures, the (2-2) average sequence length decreases with the global conversion. At the end of the reaction, structures consisting of very large styrene chains interrupted by the addition of an isolated BDMA double bond are predicted. These results allow explaining the formation of very long chains of St (high sequence length), that look like homopolymerized St at later stages of the copolymerization reaction, as it has been proposed in the literature.¹⁷⁻²¹

CONCLUSIONS

A modified terminal copolymerization model, describing the variation of the reactivity ratios with conversion, has been applied successfully to analyze the copolymerization reaction between St and BDMA. Initial St and BDMA reactivity ratios and their evolution with conversion were determined, as the only fitting parameters appearing in the inte-

grated form of the copolymerization equation, via a nonlinear least squares optimization. The results indicate that St reactivity ratio increases continuously and exponentially with the overall reaction conversion, while that of BDMA decreases linearly. These behaviors are originated by diffusion and topological restrictions upon the reactivity of St and BDMA double bonds. Changes in the reactivity ratios during reaction are the cause of the impossibility to achieve a classical azeotropic behavior in the sense of the Lewis-Mayo copolymerization theory.

The proposed dependence of the St and BDMA reactivity ratios with the global copolymerization conversion provides a consistent fitting of the experimental St and BDMA conversion results throughout the reaction, even at high conversion values where intense diffusion and topological restrictions are present. The fitting R and S parameters appearing in the reactivity ratio expressions were almost invariant with the initial concentration of comonomers, in the studied range. This feature allows simulating the copolymerization behavior of any mixture, in this concentration range, using the same parameter values.

The model predicts that the concentration of St double bonds added to the copolymer increases during the whole reaction, while that of BDMA double bonds diminishes. This behavior is due to the continuous increase of the St reactivity ratio and the linear reduction of the BDMA one during the copolymerization reaction. At the end of the reaction, structures consisting of very long St chains interrupted by the addition of an isolated BDMA double bond are predicted.

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References

- Levchik, F. L.; Si, K.; Levchik, S. V.; Camino, G.; Wilkie, C. A. *Polym Degrad Stab* 1999, 65, 395.
- Uhl, F. M.; Levchik, G. F.; Levchik, S. V.; Dick, C.; Liggit, J. J.; Snape, C. E.; Wilkie, C. A. *Polym Degrad Stab* 2001, 71, 317.
- Åström, B. T. *Manufacturing of Polymer Composites*; Chapman and Hill: London, 1997; p 86.
- Dušek, K. *Polym Gels Networks* 1996, 4, 383.
- Dušek, K.; Dušková-Smrčková, M. *Prog Polym Sci* 2000, 25, 1215.
- Okay, O.; Kurz, M.; Lutz, K.; Funke, W. *Macromolecules* 1995, 28, 2728.
- Sandner, B.; Kammer, S.; Wartewig, S. *Polymer* 1996, 37, 4705.
- Tirrell, D. A. *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1986; 4: p 192.
- Newman, R. H.; Patterson, K. *Polymer* 1996, 37, 1065.
- Batch, G. L.; Macosko, C. W. *J Appl Polym Sci* 1992, 44, 1711.
- Muzundar, S. V.; Lee, L. J. *Polym Eng Sci* 1991, 31, 1647.
- Ng, H.; Manas-Zloczower, I. *Polym Eng Sci* 1989, 29, 1097.

13. Ganem, M.; Mortaigne, B.; Bellenger, V.; Verdu, J. *J Macromol Sci Pure Appl Chem* 1993, 30, 829.
14. Scott, T. F.; Cook, W. D.; Forsythe, J. S.; Bowman, C. N.; Berchtold, K. A. *Macromolecules* 2003, 36, 6066.
15. Rosario, A. C.; Burts-Cooper, E.; Riffle, J. S. *Polymer* 2007, 48, 1203.
16. Dua, S.; Mccullough, R. L.; Palmese, G. R. *Polym Compos* 1999, 20, 379.
17. Brill, R. P.; Palmese, G. R. *J Appl Polym Sci* 2000, 76, 1572.
18. Rey, L.; Galy, J.; Sautereau, H. *Macromolecules* 2000, 33, 6780.
19. Rey, L.; Duchet, J.; Galy, J.; Sautereau, H.; Vouagner, D.; Carrion, L. *Polymer* 2002, 43, 4375.
20. Guo, Z.; Sautereau, H.; Kranbuehl, D. E. *Macromolecules* 2005, 38, 7992.
21. Mosiewicki, M. A.; Schroeder, W. F.; Leite, F. L.; Hermann, P. S. P.; Curvelo, A. A. S.; Aranguren, M. I.; Borrajo, J. *J Mater Sci* 2006, 41, 6154.
22. Mayo, F. R.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.
23. Odian, G. G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991.
24. Elias, H. -G. *Macromolecules: Synthesis, Materials, and Technology*, 2nd ed.; Plenum Press: New York, 1984; Vol. 2.
25. Stevenson, J. F. *Polym Eng Sci* 1986, 26, 746.
26. Auad, M. L.; Aranguren, M. I.; Borrajo, J. *Polymer* 2000, 41, 3317.
27. Aguilar, M. R.; Gallardo, A.; Fernández, M.; San Roman, J. *Macromolecules* 2002, 35, 2036.
28. Taylor, J. R. *An Introduction to Error Analysis*; 2nd ed.; University Science Books: Sausalito, CA, 1982.
29. Draper, N. R.; Smith, H. *Applied Regression Analysis*, Shewhart, W. A., Wilks, S. S., Eds. 2nd ed.; Wiley: New York, 1981.
30. Scott, T. F.; Cook, W. D.; Forsythe, J. S. *Polymer* 2002, 44, 671.
31. Dell'erba, R.; Martuscelli, E.; Musto, P.; Ragosta, G. *Polym Networks Blends* 1997, 7, 1.
32. Huang, Y. J.; Leu, J. S. *Polymer* 1993, 34, 295.
33. Marroyo, L. M.; Ramis, X.; Salla, J. M. *J Appl Polym Sci* 2003, 89, 3618.