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Comparative Study of the Copolymerization Kinetics of Mono and Divinylbenzyl *p-tert*-Butylcalix[4]arene Derivatives and Styrene

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A study of the copolymerization kinetics of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p-tert*-butylcalix[4]-arene (1) and 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p-tert*-butylcalix[4]arene (2) with styrene (St) was undertaken. The radical copolymerizations were carried out in THF in the presence of benzoyl peroxide at 75°C for a certain period. Six molar feed ratios, ranging from 1:1 to 1:20 (1 or 2 to St), were used to calculate the reactivity parameters. The copolymer composition was determined by FT-IR spectroscopy using a Beer's law plot obtained from the corresponding homopolymers. The reactivity ratio calculations were performed with the linearization methods of Fineman-Ross (F-R) and Kelen-Tüdös (K-T), assuming the validity of the so-called terminal model. In the copolymerization of the monoene 2, similar reactivity ratios were found for the comonomers (*ca.* 1.2; K-T). On the other hand, the reactivity ratios calculated for the copolymerization of 1 with St yielded $r_{St} = 0.67$ and $r_{calix} = 3.0$ (K-T method). The higher reactivity of monomer 1 as compared to styrene is discussed in connection with our previously postulated cyclocopolymerization route.

Keywords: Calixarene; Copolymerization; Kinetics; Reactivity Ratios; Cyclopolymerization

INTRODUCTION

A growing interest has emerged in recent years in the field of polymeric materials containing calixarenes, owing to their potential usefulness in several areas of host-guest chemistry [1]. Practical applications and fundamental studies regarding their use as sensors, non-linear optic materials and devices for selective sorption of ions and neutral molecules have been reported recently [2–8]. Calixarene-based polymers have been prepared either through its immobilization on an existing polymeric matrix [9–13] or *via* copolymerization reactions of a properly functionalized calixarene monomer, using linear step-growth polymerization [14–17] or radical addition reactions [18–22].

In line with the last synthetic route, we have been developing new functional calixarene monomers and studying their behavior under conditions of free radical polymerization. Previous work had shown that when the radical polymerization of styrene was carried out in the presence of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p-tert*-butylcalix[4]arene (**1**), a bifunctional calix[4]arene monomer bearing two *syn-nom* vinylbenzyl polymerizable groups in the lower rim, new soluble and cross-linked polymeric materials were obtained, using the suspension polymerization technique [23]. Analysis of the copolymer composition by ^{1}H NMR showed that a higher incorporation of calixarene **1** had occurred, pointing to a fairly higher reactivity of the monomer **1** as compared to styrene. On the other hand, the copolymerization of 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p-tert*-butylcalix[4]arene (**2**) with styrene, under analogous conditions, yielded a copolymer whose composition (^{1}H NMR analysis) was similar to that of the comonomers in the feed. This was interpreted as a result of the comparable reactivity of the monomers involved [24].

Cyclocopolymerization was one of the routes postulated to account for the former result, involving an intramolecular addition between the two benzyl-vinylic sub-units of **1** and an intermolecular step

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either with another calixarene molecule or with styrene [23].

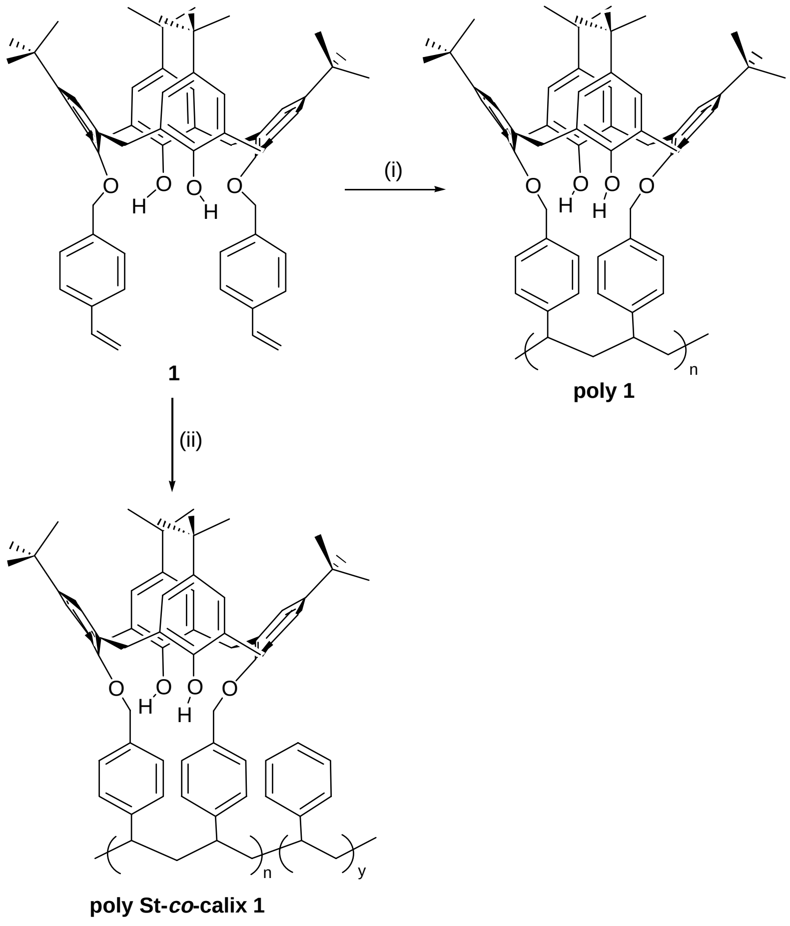
In order to further co-substantiate the proposal and gain a deeper insight into the kinetics and the mechanistic aspects associated with these copolymerizations, the present study was undertaken.

RESULTS AND DISCUSSION

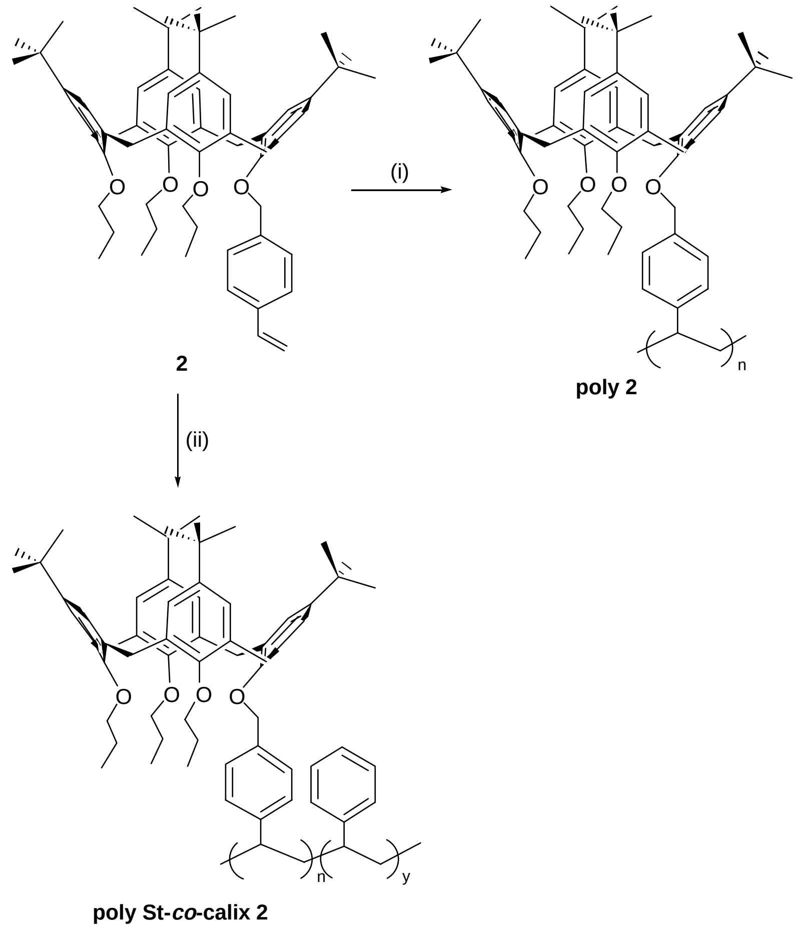
The divinylbenzyl (**1**) and monovinylbenzylcalix[4]-arene (**2**) derivatives used as monomers were prepared from *p-tert*-butylcalix[4]arene as reported elsewhere [23]. The conformational assignments for both compounds were made after inspection of the bridging methylene resonances in their ^{1}H NMR spectra. For monomer **1** (Scheme 1), the presence of two sets of doublets at 3.28 and 4.29 ppm, with a $\Delta\delta$ between the *exo* and *endo* protons of 1.01 ppm, uniquely define its distal-cone conformation [25–27]. The cone structure of **2** (Scheme 2) was established following identical reasoning (three pairs of doublets (2:1:1 ratio) at 3.08, 4.37 and 4.40, with $\Delta\delta = 1.305 \pm 0.015$ ppm).

HOMOPOLYMERIZATION OF CALIXARENES 1 AND 2

The homopolymerizations of compounds **1** and **2** were carried out as depicted in Scheme 1 (i) and Scheme 2 (i). Soluble polymers were obtained in all instances in good yields (Table I). The analysis of the ^{1}H NMR spectra of the polymers showed that the vinylic protons observable at 5.28, 5.78 and 6.76 ppm in the former monomer were absent in the spectrum of **poly 1**; the same result was found for **poly 2** (5.26, 5.77 and 6.76 ppm for **2**). Inspection of the FT-IR spectra also revealed that the vinylic stretching vibrations appearing at 1633–1629 cm^{-1} (C=C stretching) and 907–906 cm^{-1} (=CH$_2$ out-of-plane deformation) in the spectra of **1** and **2** were both absent in spectra of the homopolymers. The different molecular weights of **poly 1**, **poly 2** and **poly St** shown in Table I reflect, more than any other factor, the amount of initiator used in each experiment. Indeed, when monomer **1** was polymerized using a larger amount of BPO (13.5 mol%), a M_n of 15700 gmol^{-1} ($M_w/M_n = 1.74$) was obtained. Conversely, the homopolymerization of **1** with 0.5 mol% of BPO yielded a polymer with a M_n of 53500 gmol^{-1}



SCHEME 1 (i) BPO in THF at 75°C; (ii) idem, styrene.



SCHEME 2 (i) BPO in THF at 75°C; (ii) idem, styrene.

($M_w/M_n = 2.08$). Under the conditions described in Table I and those aforementioned, unimodal distributions were found in the GPC profiles of the three homopolymers. In general, this is indicative that chain branching reactions do not occur to a major extent [28]. This observation is of particular relevance in relation to **poly 1**, which, due to the bifunctional nature of the monomer, could have been engaged in branching or crosslinking reactions. However, only soluble polymers with high degrees of polymerization were obtained, even at high conversions (up to 90%). This led to the proposal of a cyclopolymerization route to **poly 1** [Scheme 1 (i)].

TABLE I Radical homopolymerization of calix[4]arenes **1**, **2** and **St** in THF[a]

Polymer	[BPO] (mol%)	[Monomer] (molal)	Yield (%)[b]	M_n (PDI)[c]
Poly 1	1.0	0.34	82.3	21500 (1.60)
Poly 2	13.5	0.15	59.4	9300 (1.23)
Poly St	0.5	3.05	70.8	27900 (1.71)

[a] Typical conditions: monomer **1** or **2** (296.1 mg, 0.336 and 0.332 mmol, respectively) or styrene (0.78 ml, 6.78 mmol), BPO, 75°C, 24 h (see Experimental). [b] Gravimetrically determined yield of isolated polymer. [c] The number-average molecular weight (M_n) and polydispersity index ($PDI = M_w/M_n$) were determined by GPC in THF at 35°C, using monodisperse polystyrene standards.

It is worth mentioning that when prior attempts were made to radically homopolymerize calix[4]arenes possessing one polymerizable group (acryloyl) attached to the lower rim [18] or to the upper rim [20], only oligomeric materials (pentamers and hexamers) were produced. The occurrence of steric hindrance, in the absence of a spacer group between the bulky calixarene units, was invoked to justify the results. Clearly, this does not apply to the present results.

For the purpose of reactivity ratios calculation of the copolymerization of calix[4]arene **1** and **2** with **St** (Scheme 1(ii) and Scheme 2(ii)), a Beer's law plot was produced from appropriate pairs of homopolymers using FT-IR spectroscopy. Using the ratio of the areas of the bands (out-of-plane bending) peaking at 818 cm^{-1} (**poly 1**) and 699 cm^{-1} (**poly St**) and 870 cm^{-1} (**poly 2**) and 757 cm^{-1} (**poly St**), two calibration curves (ten points each with two determinations per each concentration) were obtained. The best fit equations generated through linear least squares analysis were $y = 0.522x + 0.157$ ($R^2 = 0.992$) for **poly St - poly 1** and $y = 0.673x + 0.132$ ($R^2 = 0.992$) for **poly St - poly 2**, where x represents the actual molar polymer ratio (0 to 20; **poly St**:**poly calix**) and y is the ratio of the areas (**poly St**:**poly calix**) referred to above.

COPOLYMERIZATION KINETICS

Under steady state conditions and assuming the validity of the so-called terminal model, the Mayo-Lewis copolymerization Eq. (1) describes the behavior of a copolymer system [29]:

$$d[M_1]/d[M_2] = [M_1]/[M_2].\{r_1[M_1] + [M_2]\}/\{[M_1] + r_2[M_2]\} \quad (1)$$

where M_1 and M_2 are the two comonomers and r_1 and r_2 are the monomer reactivity ratios of the two types of radicals involved ($M_1^{\cdot}$ and $M_2^{\cdot}$), defined by the expressions:

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21}.$$

Here k_{11} and k_{12} refer to the rate constants of the propagation reactions involving a radical $M_1^{\cdot}$ at the end of a growing chain adding to the monomer M_1 and M_2, respectively. k_{22} and k_{21} are the corresponding rate constants for the addition of the growing radical $M_2^{\cdot}$ to M_2 and M_1.

Reactivity ratios have been determined by several methods [29–31]. All copolymerizations present a drift in the monomer ratio as the reaction proceeds. It is normally accepted that linearized methods can be used up to 10% of conversion, providing that the reactivity ratios of the monomer pairs involved do not greatly differ. Methods that take into account the compositional drift have been reported [32].

The Fineman-Ross (F-R) and the Kelen-Tüdös (K-T) methods were applied in the present work. Both are linearized forms of the Mayo-Lewis copolymerization equation, which can be expressed by the following formalisms.

Being $x = [M_1]/[M_2]$ the molar ratio of monomers in the feed and $y = [m_1]/[m_2]$ the molar ratio of monomer units in the copolymer, the F-R plot graphs G *vs* F in the form shown in Eq. (2):

$$x(y-1)/y = r_1(x^2/y) - r_2 \quad (2)$$

with $x\,(y\,\text{-}1)/y = G$ and $x^2/y = F$.

The plot gives a straight line whose slope is r_1 and whose intercept is $-r_2$.

The K-T method was developed later and an additional parameter, α (vide infra), was added in order to overcome the disadvantage of the F-R method related to the different weights assumed by the single data points used to calculate the regression line [33]. Eq. (3) expresses the K-T formalism:

$$\eta = r_1\,\xi - r_2/\alpha(1-\xi) \quad (3)$$

where η and ξ are:

$$\eta = G/\alpha + F \quad \xi = F/\alpha + F$$

A plot of η vs ξ should give a straight line in which the intercepts at $\xi = 0$ and at $\xi = 1$, correspond to $-r_2/\alpha$ and to r_1, respectively. The auxiliary parameter α is calculated from the Eq. (4) and is used to uniformly distribute the data points in the domain of ξ.

$$\alpha = [F_{\text{lowest}}F_{\text{highest}}]^{1/2} \quad (4)$$

EVALUATION OF THE REACTIVITY RATIOS OF THE COPOLYMERIZATION OF St (M_1) AND CALIXARENE 1 (M_2)

The time for each copolymerization was set between 1.5 h to 2.5 h in order to keep the conversions less than 10 wt%, based on the conversion rates previously obtained for the corresponding homopolymers. Six molar feed ratios, ranging from 1:1 to 1:20 (**1** to **St**), were used to calculate the reactivity parameters (Table II). The copolymer composition was determined by FT-IR spectroscopy, using the Beer's law plot generated for the homopolymers (**poly 1** and **poly St**) at various concentrations (see above). By measuring the ratio of the areas of the bands peaking at 820 cm^{-1} and 698 cm^{-1}, corresponding to those that appear in the spectra of **poly 1** and **poly St**, respectively, the molar ratios (m_1/m_2) of the monomer units in the copolymer were determined (Table II).

Figure 1 shows the F-R plot obtained from the data of Table II. Similarly, the K-T plot is presented in Figure 2.

TABLE II Copolymerization data of **St** (M_1) and calixarene **1** (M_2)[a]

Entry	Feed $[M_1]/[M_2]$	Copolymer $[m_1]/[m_2]$	Reaction Time (hl) (h)	Yield (%)[b]	M_n (PDI)[c]	F-R parameters G	F-R parameters F	K-T parameters[d] η	K-T parameters[d] ξ
1	1.01	0.433	1.5	5.6	25600 (1.53)	−1.32	2.34	−0.1235	0.219
2	3.56	1.97	2.5	8.1	16500 (1.85)	1.755	6.43	0.119	0.435
3	4.99	2.50	1.5	4.1	18300 (2.29)	2.99	9.97	0.163	0.544
4	7.02	3.84	2.5	8.3	20300 (2.22)	5.19	12.8	0.245	0.605
5	15.0	9.09	1.5	4.4	13600 (2.78)	13.3	24.6	0.404	0.747
6	20.0	13.4	1.5	3.1	28000 (2.05)	18.5	29.8	0.485	0.781

[a] Typical conditions: Styrene (0.204–1.35 mmol), calixarene **1** (0.203–0.0675 mmol), BPO (1.0 wt%), THF (0.7 ml), 75°C. [b] Gravimetrically determined yield of isolated polymer. [c] M_n and polydispersity index (PDI = M_w/M_n) as determined by GPC. [d] $\alpha = [F_{\text{lowest}}F_{\text{highest}}]^{1/2} = 8.35$.

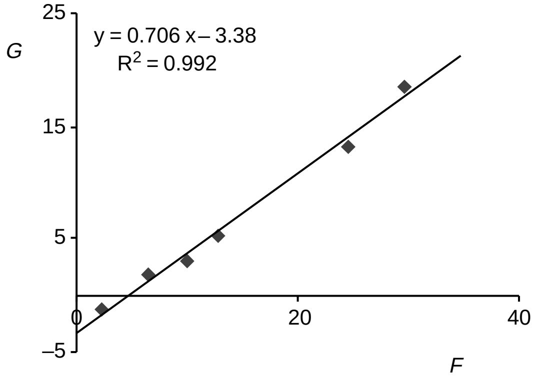


FIGURE 1 Fineman-Ross plot for **St**-*co*-calixarene(**1**) copolymers.

The two methods yielded similar values for the reactivity ratios: $r_1 = 0.71$ (F-R) and 0.67 (K-T) and $r_2 = 3.38$ (F-R) and 3.00 (K-T). These values mean that the rate of adding the calixarene unit **1** to a growing chain is always higher ($r_2/r_1 = 4.5$; K-T), as compared to the styrene addition, irrespective of the nature of the terminal radical. This may be explained on the basis of the relative activation energies of both competing processes. The intermediates that are formed after the attack of the propagating radicals (St or calix type) to the calixarene monomer **1** are further stabilized comparatively to those that resulted from the addition of the same radicals to **St**, due to electronic stabilizing effects originated from the neighboring vinylbenzyl group. Such favorable spatial and electronic interactions attained by the distal 4-vinylbenzyl groups, or by the intramolecular vinylic double bond and the thus formed reactive center, during the course of polymerization, should be credited to the constrained environment generated by the calixarene moiety in its cone conformation. The intramolecular cyclization step, which leads to the proposed cyclocopolymer, is in turn favored in entropic grounds, as compared to an intermolecular addition reaction either to a calixarene or to a styrene monomer, since a smaller decrease in entropy is expected for the former process [34].

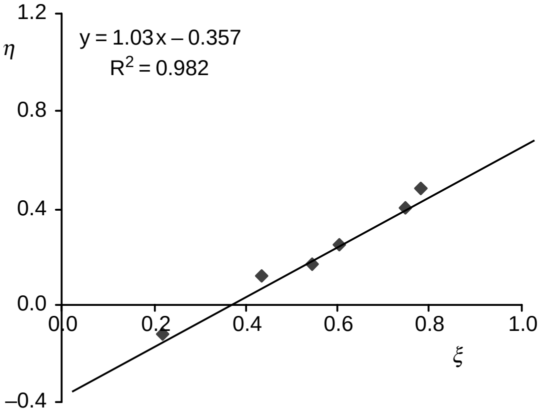


FIGURE 2 Kelen-Tüdös plot for **St**-*co*-calixarene(**1**) copolymers; $\alpha = [F_{\text{lowest}}F_{\text{highest}}]^{1/2} = 8.35$.

EVALUATION OF THE REACTIVITY RATIOS OF THE COPOLYMERIZATION OF St (M_1) AND CALIXARENE 2 (M_2)

Identical procedures to those reported above were followed in the calculation of the reactivity ratios of the copolymerization of **St** (M_1) and calixarene **2** (M_2). The copolymer composition was determined using the bands peaking at 869 cm^{-1} and 757 cm^{-1} for the measurements. Table III presents the data used in the calculation.

Plots of the two methods are shown in Figures 3 and 4.

The reactivity ratios obtained from the two methods are roughly the same: $r_1 = 1.26$ (F-R) and 1.23 (K-T) and $r_2 = 1.44$ (F-R) and 1.23 (K-T). Contrary to the former copolymerization system, the growing chains of either type of radical active site (M_1 and M_2 radicals) showed a similar reactivity towards the monomers M_1 and M_2, albeit a perceptible propensity to add to their own monomer. This behavior is justifiable by the similar nature of the reactive centers involved in the copolymerization. In this case, a nearly random distribution of the monomers should have resulted and the copolymer composition at any instant should resemble the initial molar ratio of the monomers.

TABLE III Copolymerization data of **St** (M_1) and calixarene **2** (M_2)[a]

Entry	Feed $[M_1]/[M_2]$	Copolymer $[m_1]/[m_2]$	Reaction Time (h)	Yield[b] (%)	M_n[c] (PDI)	F-R parameters		K-T parameters[d]	
						G	F	η	ξ
1	3.56	3.92	1.5	10.1	12900 (1.74)	2.65	3.235	0.255	0.311
2	5.00	6.15	2.5	3.4	17000 (1.78)	4.19	4.06	0.373	0.362
3	7.48	7.72	2.5	6.0	22500 (2.09)	6.51	7.24	0.452	0.503
4	9.99	12.6	2.5	5.6	15500 (1.73)	9.19	7.90	0.610	0.525
5	15.0	17.3	2.5	3.6	19500 (1.70)	14.2	13.1	0.699	0.647
6	20.0	25.2	2.5	5.4	15200 (1.67)	19.2	15.8	0.835	0.689

[a] Typical conditions: Styrene (0.565–1.35 mmol), calixarene **2** (0.159–0.0674 mmol), BPO (1.0 wt%), THF (0.7 ml), 75°C. [b] Gravimetrically determined yield of isolated polymer. [c] M_n and polydispersity index (PDI = M_w/M_n) as determined by GPC [d] $\alpha = [F_{\text{lowest}}F_{\text{highest}}]1/2 = 7.15$.

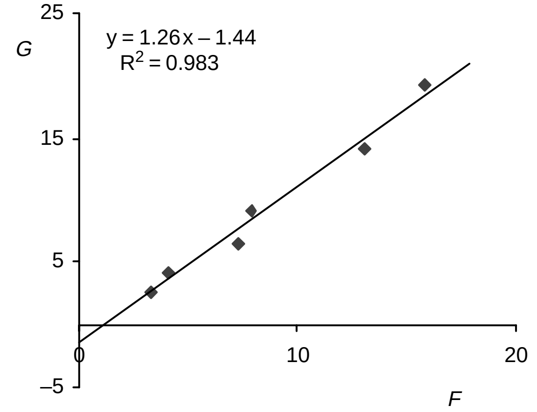


FIGURE 3 Fineman-Ross plot for **St**-*co*-calixarene(**2**) copolymers.

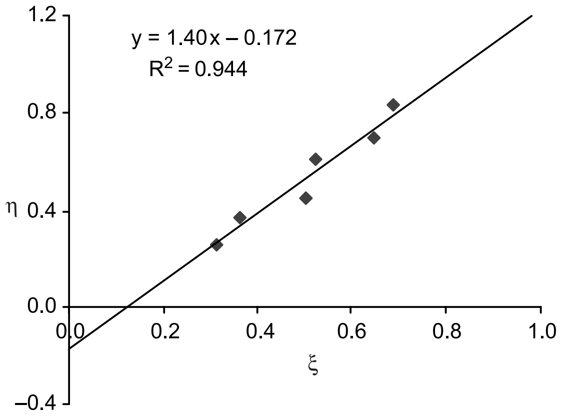


FIGURE 4 Kelen-Tüdös plot for **St**-*co*-calixarene(**2**) copolymers; $\alpha = [F_{\text{lowest}}F_{\text{highest}}]^{1/2} = 7.16$.

CONCLUSIONS

The calculation of the reactivity ratios of the systems divinylbenzylcalixarene **1**:**St** and the monoene counterpart **2**:**St** allowed a mechanistic interpretation of the results and additional supporting evidence for the cyclocopolymerization route proposed for the former system.

It is argued that the higher polymerizability of the calix[4]arene **1** should be related to the favorable spatial and electronic interactions attained by the *syn*-distal 4-vinylbenzyl groups and its radical derivatives during the course of polymerization, due to the structural arrangements of the pendant substituents imposed by the calixarene moiety.

EXPERIMENTAL

Materials and Methods

Melting points were recorded on a Büchi 530 apparatus and are reported uncorrected. Infrared spectra (FT-IR) were measured on a Nicolet Impact 400D spectrometer as KBr pellets (transmission mode), at a resolution of 2 cm^{-1}. Proton nuclear magnetic resonance spectra (^{1}HNMR) were recorded on a Brüker ARX 400 (400 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard; *J* values are given in Hz. Elemental analyses were performed at the Microanalyses Services of Universidad de Vigo (C.A.C.T.I.). Gel permeation chromatography (GPC) analysis was performed on a Jasco Liquid Chromatograph system equipped with a Jasco Refractive Index Detector 2031 Plus and a Jasco UV Absorption Detector 1575, using PSS SDV columns (10^3 and 10^5 Å) and THF as eluent at 35°C. Calibration was done with monodisperse polystyrene standards.

All reagents and solvents were reagent grade and were purified and dried by standard methods. Analytical thin-layer chromatography (TLC) was performed on E. Merck kieselgel 60, F-254 silica-gel 0.2 mm thick plates. *p*-*Tert*-butylcalix[4]arene and 25,26,27-tripropoxy-28-hydroxy-*p*-*tert*-butylcalix[4]-arene were synthesized according to reported methods [35,36]. 4-Vinylbenzyl chloride (Fluka, 90%) was used as received. Benzoyl peroxide (BPO; Merck) was previously recrystallised from $CHCl_3$–MeOH. The polymerization yields were determined gravimetrically.

Characterization of Calix[4]arene Derivatives

The calix[4]arene derivatives **1** and **2** used in this study were prepared according to previously reported procedures [23]. Details pertaining their characterization are as follows.

25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-p-tert-butylcalix[4]arene (1)

mp 203–205°C; ν_{max}/cm^{-1} 3430, 1629, 993, 907; δ_H 0.95 (18H, s, $C(CH_3)_3$), 1.29 (18H, s, $C(CH_3)_3$), 3.28 (4H, d, $ArCH_2Ar$, *J* 13.1), 4.29 (4H, d, $ArCH_2Ar$, *J* 13.1), 5.05 (4H, s, $ArOCH_2Ar$), 5.28 (1H, d, —CH=C*H*H, *J* 10.9), 5.78 (1H, d, —CH=CH*H*, *J* 17.6), 6.76 (1H, dd, —C*H*=CH_2, *J* 10.9 and *J* 17.6), 6.80 (4H, s, Ar*H*), 7.05 (4H, s, Ar*H*), 7.32 (2H, s, ArO*H*), 7.41 and 7.63 (4H each, d each, vinyl-Ar*H*, *J* 8.0). Anal. Calcd. for $C_{62}H_{72}O_4$: C, 84.50; H, 8.24. Found: C, 84.79; H, 8.24.

25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-p-tert-butylcalix[4]arene (2)

mp 127–130°C; ν_{max}/cm^{-1} 1633, 907; δ_H 0.77 (6H, t, —CH_2CH_3, *J* 7.4), 0.96 (9H, s, $C(CH_3)_3$), 0.99 (9H, s, $C(CH_3)_3$), 1.01 (3H, t, —CH_2CH_3, *J* 7.5), 1.21 (18H, s, $C(CH_3)_3$), 1.76–2.04 (6H, m, —CH_2CH_3), 3.08 (4H, d, $ArCH_2Ar$, *J* 12.6), 3.69 (2H, t, —OCH_2,CH_2 OCH_2CH *J* 7.2), 3.78 (4H, t, —OCH_2CH_2—, *J* 7.8), 4.37 (2H, d, $ArCH_2Ar$, *J* 12.4), 4.40 (2H, d, $ArCH_2Ar$, *J* 12.4), 4.78 (2H, s, $ArOCH_2Ar$), 5.26 (1H, d, —CH=C*H*H, *J* 10.8), 5.77 (1H, d, —CH=CH*H*, *J* 17.6), 6.58 (2H, s, Ar*H*), 6.58

(2H, s, Ar*H*), 6.76 (1H, dd, $-\mathrm{C}H{=}\mathrm{CH}_2$, *J* 10.8 and *J* 17.7), 6.89–6.98 (4H, m, Ar*H*), 7.41 and 7.45 (4H, d each, vinyl-Ar*H*, *J* 8.1). Anal. Calcd. for $C_{62}H_{82}O_4.H_2O$: C, 81.89; H, 9.31. Found: C, 81.41; H, 9.30.

Homopolymerization of 1, 2 and St

General Procedure

Benzoyl peroxide was added to a solution of the monomer (**1, 2** or **St**; see Table I) in dried THF contained in a tube, under argon. After sealing, the reaction mixture was degassed by three freeze-pump-thaw cycles and the contents were magnetically stirred and heated at 75°C (pre-heated oil-bath). After 24 h, the reaction mixture was quenched in an ice bath and the solvent evaporated. The residue was taken in a minimum amount of dichloromethane and precipitated in methanol; this operation was repeated until no free monomer was detectable in the TLC or GPC of the samples. The polymers were dried in a vacuum oven at 65°C.

Poly 1. Obtained as a colorless solid in 82.3%, using 1.0 mol% of BPO; ν_{max}/cm^{-1} 3367, 1600, 871, 818; δ_H 1.12 (18H, s, $\mathrm{C}(\mathrm{C}H_3)_3$), 1.24 (18H, s, $\mathrm{C}(\mathrm{C}H_3)_3$), 1.25–2.25 (6 H, m, $-\mathrm{CH(Ar)C}H_2-$, $-\mathrm{C}H\mathrm{(Ar)CH}_2-$), 3.32 (4H, bs, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.38 (4H, bs, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.72 (4H, bs, $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.40, 6.99, 7.36 (16 H, bs, Ar*H*), 8.31 (2H, s, ArO*H*). Anal. Calcd. for $(C_{62}\,H_{72}O_4.H_2O)_n$: C, 82.80; H, 8.29. Found: C, 82.70; H, 8.20.

Poly 2. Isolated in 59.4% as a colorless solid, using 13.5 mol% of BPO; ν_{max}/cm^{-1} 1603, 1582, 870; δ_H 0.61 (9 H, bs, $-\mathrm{CH_2CH_2C}H_3$), 0.88 (18 H, s, $-\mathrm{C}(\mathrm{C}H_3)_3$), 1.23 (18 H, s, $-\mathrm{C}(\mathrm{C}H_3)_3$), 1.40–2.00 (3 H, m, $-\mathrm{C}H\mathrm{(Ar)CH}_2-$, $-\mathrm{CH(Ar)C}H_2-$), 1.83 (6 H, m $-\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.96 (4H, bs, $\mathrm{ArC}H\mathrm{(H)Ar}$), 3.67 (6H, m, $-\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.33 (4H, bs, $\mathrm{ArCH}(H)\mathrm{Ar}$), 4.62 (2H, bs, $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.51, 6.96 (12 H, m, Ar*H*). Anal. Calcd. for $(C_{62}\,H_{82}O_4.H_2O)_n$: C, 81.89; H, 9.31. Found: C, 82.11; H, 9.02.

Preparation of Poly(styrene-*co*-calixarene(1 or 2))

The procedure described above was generally followed. The feeding molar ratios of comonomers used for the reactivity ratios study are reported in Table II and Table III. BPO was used at a concentration of 1.0 wt% of the total weight of the monomers throughout the experiments. The reaction time for each copolymerization was set between 1.5 h to 2.5 h in order to keep the conversions under 10 wt% (gravimetrically determined). Preparative runs with a selected molar ratio of comonomers (1:20, calix **1**:**St** or 1:10, calix **2**:**St**; feed) were extended to a 24 h period. The resulting copolymers were characterized as follows:

Poly(styrene-co-calixarene 1)

Obtained as a colorless solid in 60.0% (yield corrected from ^{1}H NMR data); ν_{max}/cm^{-1} 3378, 1602, 1583, 872, 820, 757, 698; δ_H 0.95, 1.13, 1.27 ($-\mathrm{C}(\mathrm{C}H_3)_3$), 1.10–1.60 (m, $-\mathrm{CH(Ar)C}H_2-$), 1.60–2.00 (m, $-\mathrm{C}H\mathrm{(Ar)CH}_2-$), 3.37 (bs, $\mathrm{ArC}H\mathrm{(H)Ar}$), 4.43 (bs, $\mathrm{ArCH}(H)\mathrm{Ar}$), 4.79 (bs, $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.20–6.80 (m, Ar*H*), 6.80–7.20 (m, Ar*H*; ArO*H*); ^{1}H NMR analysis showed a molar ratio of *ca.* 1:13 (calix **1**:**St**) of the monomeric units in the copolymer. Anal. Found: C, 88.57; H, 8.05.

Poly(styrene-co-calixarene 2)

Obtained as colorless solid in 48.0%; ν_{max}/cm^{-1} 1602, 1583, 869, 757, 698; δ_H 0.69 (bs, $-\mathrm{CH_2CH_2C}H_3$), 0.75–1.66 (several m, $-\mathrm{C}(\mathrm{C}H_3)_3$, $-\mathrm{CH_2CH_2C}H_3$, $-\mathrm{CH(Ar)C}H_2-$), 1.66–2.20 (m, $-\mathrm{C}H\mathrm{(Ar)CH}_2-$, $-\mathrm{CH_2C}H_2\mathrm{CH_3}$), 3.10 (bs, $\mathrm{ArC}H\mathrm{(H)Ar}$), 3.72 (bs, $-\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.39 (bs, $\mathrm{ArCH}(H)\mathrm{Ar}$), 4.71 (bs, $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.24–6.78 (m, Ar*H*), 6.81–7.20 (m, Ar*H*); ^{1}H NMR analysis showed a molar ratio of *ca.* 1:10 (calix **2**:**St**) of the monomeric units in the copolymer. Anal. Found: C, 86.95; H, 8.53.

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