Influence of temperature on butyl acrylate – styrene copolymerization parameters

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Butyl acrylate (BA) – styrene (ST) copolymerization was carried out in bulk without any free-radical initiator at 110, 150 and 170°C. The Kelen–Tudos (K–T) transformation of comonomers–copolymer composition data shows that the copolymerization can be sufficiently described by a terminal copolymerization model. Reactivity ratios for BA (r_1) and ST (r_2) were estimated by the K–T method as well as by the error-in-variables method. Together with previous reports on BA–ST copolymerization at 50 and 60°C, these values of r_1 and r_2 served to find the Arrhenius relationships: $\ln r_1 = 1.3510 - 1034.1/T$, and $\ln r_2 = 0.05919 - 131.6/T$, where T is absolute temperature. Thus, although r_1 can be strongly affected by temperature, r_2 is practically temperature insensitive. This can be explained by the activation energy differences between homo- and cross-propagations (8.6 and 1.1 kJ mol^{-1}, respectively). Effect of conversion on copolymer and comonomers composition is also discussed.

(Keywords: copolymerization; butyl acrylate; styrene; copolymerization reactivity ratios; temperature effect)

INTRODUCTION

In the copolymerization of vinyl monomers, propagation is usually described by four reactions:

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1M_1\cdot \qquad (1)$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_1M_2\cdot \qquad (2)$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2M_2\cdot \qquad (3)$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_2M_1\cdot \qquad (4)$$

and reactivity ratios are defined as:

$$r_1 = k_{11}/k_{12}; \qquad r_2 = k_{22}/k_{21} \qquad (5)$$

The instantaneous composition of copolymer formed is then given[1] as:

$$y = (1 + r_1 x)/(1 + r_2/x) \qquad (6)$$

where y and x are ratios of mole fractions of monomer 1 and monomer 2 in the copolymer and the monomer mixture, respectively.

Even though extensive work to establish reactivity ratios for various pairs of monomers has been done, the effect of polymerization temperature on the reactivity ratios has usually been neglected[2]. Mayo and Walling, who in 1950[3] published a few experimental results on determining reactivity ratios at two or three different temperatures, have suggested that monomer reactivity ratios slowly approach unity as the temperature rises.

Copolymers of butyl acrylate (BA) and styrene (ST) produced at elevated temperatures might be useful as, for example, adhesives or plasticizers, but lack of information on the reactivity ratios at these temperatures makes it difficult to design such a process. On the other hand, high copolymerization rates in the initial stages of the process at high temperatures should be expected, therefore the usual procedure to find reactivity ratios would be very difficult to perform. Thus, developing the relationships between reactivity ratios and temperature for BA–ST copolymerization should enable the prediction of reactivity ratios for elevated temperatures.

Recently Kaszas *et al.*[4] carried out extensive studies of BA–ST copolymerization in bulk and in solution. However, they did not estimate the temperature effect.

The main purpose of the present work is to evaluate the temperature dependence of the BA–ST copolymerization parameters, to enable the prediction of the system reactivity at elevated temperatures.

EXPERIMENTAL

BA and ST were repeatedly washed with a 5% aqueous sodium hydroxide solution and with distilled water, dried over sodium sulphate, and distilled at reduced nitrogen pressure. The purified monomers were copolymerized in bulk using glass ampoules (5 mm o.d.). The ampoules containing monomer mixtures were degassed by repeated freezing, evacuating and thawing cycles, and then sealed off under vacuum. The polymerizations were carried out at 110, 150 and 170°C; conversion was 1.5–5.5 wt%. In addition, a few high conversion copolymers were also prepared at 170°C.

Since ST is known from its ability to initiate thermal free-radical polymerization, no free-radical initiator was applied. In this way it was possible to avoid contamination of the product by the residual catalyst and/or its decomposition products, and incorporation of the initiator into copolymer chains. Hence, further experimental steps seemed to be justified.

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To recover copolymers, post-polymerization mixtures (sometimes diluted after reaction to reduce viscosity) were poured onto Petri dishes to form thin layers, and dried under vacuum at temperatures up to 90°C for 1 week.

The copolymer compositions were determined by applying i.r. spectroscopy. Thus, the calibration curve was prepared by using mixtures of appropriate homopolymers (PBA and PST) and measuring the relative absorbance in chloroform solution in the region of the carbonyl band around 1730 cm^{-1}. (Mori[5] proved recently that this band is independent of sequence distribution and can be used for the determination of copolymer composition.) The calibration was checked at every series of copolymer composition measurements, and then by measuring the absorbance of chloroform solutions of copolymers (concentration 10 $\mathrm{mg\,ml}^{-1}$) reproducible results of BA content were obtained.

RESULTS AND DISCUSSION

As mentioned, Kaszas *et al.*[4] carried out detailed studies of BA–ST copolymerization at 50°C; they used the Kelen–Tudos (K–T) method[6] for determining copolymerization reactivity ratios, and showed that the values and confidence intervals were equivalent to those obtained by the non-linear least squares method.

To check whether the terminal copolymerization model (equations (1)–(6)) can adequately approximate our data and to obtain reactivity ratio values consistent with those of Kaszas, we started evaluation of our experimental results using the K–T method. This method is an improved extension of the Fineman–Ross graphic technique[7]. According to the K–T method, the following linear equation – obtained by the appropriate transformation of equation (6) – can be used to describe binary copolymerization data:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \qquad (7)$$

where $\xi = 1/(1 + y/x^2)$ and $\eta = (y-1)/x(1 + y/x^2)$. Adjustable parameter α serves to distribute uniformly and symmetrically the experimental points between 0 and 1, and is suitably obtained by the expression $\alpha = [(x^2/y)_{\mathrm{min}}(x^2/y)_{\mathrm{max}}]^{1/2}$ from the lowest and the highest values of x^2/y in a given experiment. If the η *versus* ξ plot is linear for a binary copolymerization, equation (6) holds and the two-parameter r_1 and r_2 model is a satisfactory approximation to describe the system.

Table 1 presents experimental x and y values for copolymerizations carried out by us at 110, 150 and 170°C, as well as η and ξ variables calculated from them. The η *versus* ξ plots for these copolymerizations can be well approximated by straight lines, which means that the terminal model is sufficient to describe our system. Since equation (7) can be rewritten as:

$$\eta = r_1\xi - (r_2/\alpha)(1 - \xi) \qquad (8)$$

it is clear that from the intercepts at $\xi = 1$ and $\xi = 0$ one can obtain r_1 and r_2 values. Kelen *et al.*[8] derived expressions to calculate the 95% confidence intervals for r_1 and r_2 values found by the K–T method. The values of reactivity ratios and confidence intervals determined by the K–T method in this work, together with the values determined by Kaszas *et al.*[4] for the copolymerization at 50°C, as well as recalculated results of Bradbury and Melville[9] for 60°C, are shown in *Table 2*. The results presented in this table imply that the temperature range 50–170°C has a distinct effect on the BA reactivity ratio (r_1), whereas the ST reactivity ratio (r_2) changes only slightly with temperature.

Table 1 Comonomer mixture and copolymer compositions and the Kelen–Tudos parameters for the BA(1)–ST(2) system at different temperatures

	BA/ST mole fraction ratios		Kelen – Tudos parameters		
Temp. (°C)	Comonomers x	Copolymer y	α	ξ	η
110	0.228	0.244	1.337	0.1376	−0.4563
	0.427	0.387		0.2607	−0.3742
	1.115	0.709		0.5671	−0.1478
	1.497	0.898		0.6512	−0.0446
	2.328	1.183		0.7740	0.0610
	3.953	1.732		0.8709	0.1613
150	0.250	0.266	2.293	0.0933	−0.2736
	0.429	0.399		0.1674	−0.2349
	1.001	0.724		0.3764	−0.1037
	2.331	1.410		0.6270	0.1102
	9.050	3.673		0.9068	0.2678
170	0.250	0.272	2.316	0.0906	−0.2638
	0.429	0.418		0.1595	−0.2163
	1.001	0.765		0.3613	−0.0847
	1.498	1.101		0.4680	0.0315
	2.331	1.370		0.6314	0.1001
	4.000	2.226		0.7563	0.2318
	9.050	3.878		0.9012	0.2866

Table 2 Values of monomer reactivity ratios for the BA(1)–ST(2) system at different temperatures[a]

Temp. (°C)	r_1	Δr_1	r_2	Δr_2	Reference	Remarks[b]
50	0.16	0.02	0.70	0.03	4	K–T
60	0.17	0.07	0.70	0.15	4,9	K–T
110	0.25	0.05	0.79	0.08	this work	K–T
	0.25	0.04	0.80	0.06	this work	EVM
150	0.34	0.06	0.79	0.11	this work	K–T
	0.34	0.06	0.78	0.07	this work	EVM
170	0.38	0.05	0.75	0.10	this work	K–T
	0.38	0.04	0.76	0.05	this work	EVM

[a] Individual 95% confidence intervals are approximately equal to $\pm\Delta r_1$, $\pm\Delta r_2$

[b] K–T, Kelen–Tudos procedure of estimation; EVM, error-in-variables method

The r_1 and r_2 values estimated by us using the K–T procedure were verified employing the error-in-variables method (EVM). This method assumes that all observations, not only those of dependent variables, are coming from some unknown true values plus measurement errors. The errors are assumed to be normally distributed. To use the method, the variance of each measurement must be estimated; details about EVM are given, for example, in refs 10 and 11. To estimate reactivity ratios, the EVM requires much more elaborate computations than the K–T method. The appropriate software was developed by Gloor[11] and was used in this work. Results of the EVM estimation of BA(1)–ST(2) reactivity ratios for 110, 150 and 170°C are shown in *Figure 1*. This figure shows joint confidence regions for r_1–r_2 values; it is highly probable that reactivity ratios for 110 and 170°C belong to different populations, which means that temperature has a significant effect on BA–ST reactivity ratios.

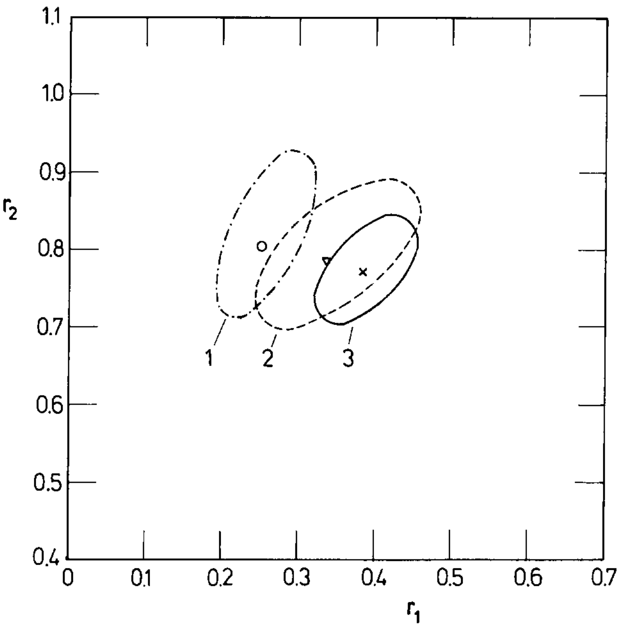

Figure 1 Reactivity ratios estimated by the error-in-variables method and their 95% confidence regions for BA(1)–ST(2) copolymerization at: 1 (○, –·–·), 110°C; 2 (▽, -----), 150°C; 3 (×, ——), 170°C

Numerical values of r_1 and r_2 estimated by the EVM together with approximate individual 95% confidence intervals are presented in *Table 2*. Comparing these results with those estimated by the K–T procedure, it is evident that there is an excellent agreement between them. Consequently, it seems to be justified to make comparisons between our determinations of reactivity ratios for temperatures 110–170°C, and those of Kaszas *et al.*[4] for BA–ST copolymerization at 50 and 60°C.

It would be instructive to visualize how a BA–ST copolymerization temperature increase from 50 to 170°C affects the relationship between the instantaneous copolymer composition and the composition of comonomers. Let us reconsider equation (6): since $y = F_1/F_2$, $x = f_1/f_2$, $F_1 + F_2 = 1$ and $f_1 + f_2 = 1$, copolymerization equation (6) can be expressed as:

$$F_1 = [(r_1 - 1)f_1^2 + f_1]/[(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2] \tag{9}$$

Figure 2 shows instantaneous content of BA units in the copolymer (F_1) as a function of BA content in the comonomer mixture (f_1) for three selected temperatures: 50, 110 and 170°C. It is evident that our experimental results are well modelled by equation (9) based on the terminal copolymerization model. It is seen that for comonomer mixtures containing more then 50 mol% BA the effect of temperature on the instantaneous copolymer composition is particularly strong: for a given comonomer composition, the higher the temperature, the more BA units can be incorporated into the copolymer. However, although the difference between BA and ST reactivity ratios is decreased with temperature increase, there may still be a significant compositional drift during batch copolymerization of BA-rich mixtures. To check how copolymer composition changes with conversion during copolymerization of an equimolar BA–ST mixture at the highest of the investigated temperatures (170°C), we carried out the batch process up to high conversions and investigated the resultant copolymer compositions.

Meyer and Lowry[12] derived an integral copolymerization equation relating molar conversion C_M of the copolymerizing system with the initial (f_{10}) and instantaneous (f_1) composition of the mixture of comonomers having r_1 and r_2 reactivity ratios:

$$C_M = 1 - (f_1/f_{10})^a[(1 - f_1)/(1 - f_{10})]^b[(f_{10} - d)/(f_1 - d)]^c \tag{10}$$

where $a = r_2/(1 - r_2)$; $b = r_1/(1 - r_1)$; $c = (1 - r_1r_2)/[(1 - r_1)(1 - r_2)]$; and $d = (1 - r_2)/(2 - r_1 - r_2)$.

From the mass balance we obtain the cumulative copolymer composition:

$$F_{1c} = [f_{10} - f_1(1 - C_M)]/C_M \tag{11}$$

Molar conversion can be recalculated into weight conversion C_w:

$$C_w = C_M[M_2 + F_{1c}(M_1 - M_2)]/[M_2 + f_{10}(M_1 - M_2)] \tag{12}$$

where M_1 and M_2 are the molar masses of comonomers.

Using these equations and equation (9), we calculated cumulative and instantaneous copolymer compositions at different weight conversions during copolymerization of the equimolar BA–ST mixture ($f_{10} = 0.5$), and compared them with F_{1c} values found experimentally. The results are presented in *Figure 3*. It is evident that the experimental F_{1c} values are in good agreement with the curve calculated theoretically on the basis of the Meyer–Lowry equation. There is no indication of unusual dependence of F_{1c} as a function of conversion (with a maximum at ~30 wt% and a minimum at ~60 wt% conversion) as reported by Johnson *et al.*[13] and Dionisio and O'Driscoll[14] for high conversion copolymerization of ST and methyl methacrylate. Our results indicate that for the equimolar BA–ST copolymerization at elevated temperatures F_{1c} values change only

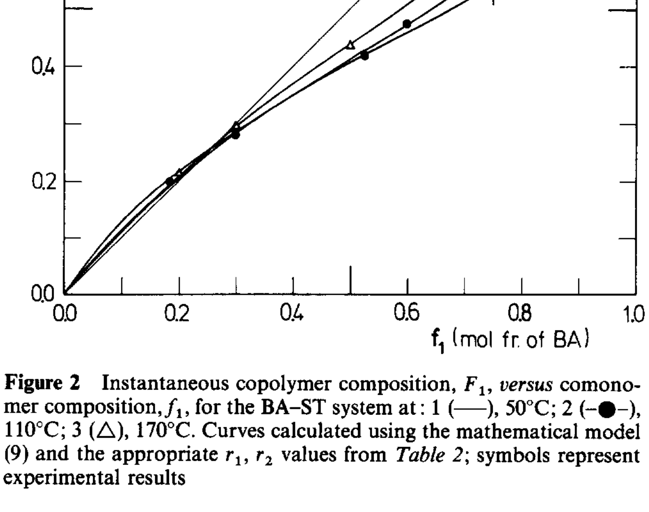

Figure 2 Instantaneous copolymer composition, F_1, *versus* comonomer composition, f_1, for the BA–ST system at: 1 (——), 50°C; 2 (-●-), 110°C; 3 (△), 170°C. Curves calculated using the mathematical model (9) and the appropriate r_1, r_2 values from *Table 2*; symbols represent experimental results

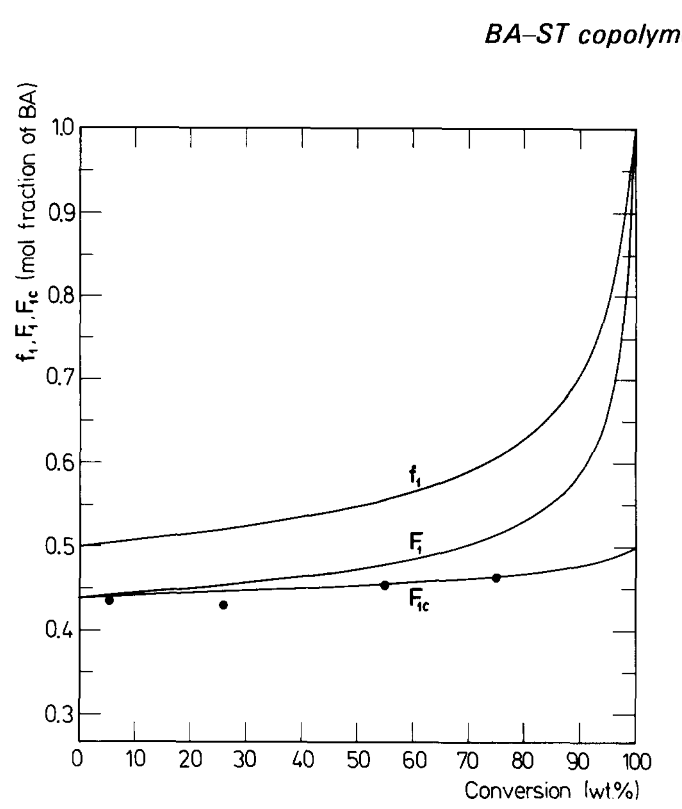

Figure 3 Variation of the cumulative copolymer composition, F_{1c}, comonomer composition, f_1, and instantaneous copolymer composition, F_1, with conversion for BA–ST = 50/50(mol%) batch copolymerization at 170°C. Symbols (●) represent the experimental F_{1c} results

slightly with conversion. Nevertheless, due to a continuous change of comonomer composition (f_1) with conversion, instantaneous composition (F_1) of the copolymer formed at, for example, 75 wt% conversion is significantly different ($F_1 = 0.515$) from F_1 of the copolymer formed at the beginning of the process ($F_1 = 0.440$), though F_{1c} has only changed from 0.44 to 0.46 mole fraction of BA units.

One can reduce this compositional drift to some extent by carrying out the copolymerization at suitably high temperatures when the difference between reactivity ratios is sufficiently small. To predict reactivity ratios at temperatures above 170°C let us consider the following: since temperature dependence of rate constants may be written as an Arrhenius equation, $k = A\exp(-E/RT)$ (where E is the activation energy, R the gas constant and T the absolute temperature), then:

$$r_1 = (A_{11}/A_{12})\exp[-(E_{11} - E_{12})/RT] \qquad (13)$$

$$r_2 = (A_{22}/A_{21})\exp[-(E_{22} - E_{21})/RT] \qquad (14)$$

Now if we let $\Delta E_1 = E_{11} - E_{12}$, $\Delta E_2 = E_{22} - E_{21}$, $A_1 = A_{11}/A_{12}$ and $A_2 = A_{22}/A_{21}$, then:

$$\ln r_i = \ln A_i - \Delta E_i/RT \qquad (15)$$

where $i = 1, 2$.

By finding parameters for this linear form of the Arrhenius equation, one can estimate differences in activation energies between homo- and cross-propagation reactions, and predict reactivity ratios for a broad range of temperatures.

Figure 4 shows $\ln r_i = f(1/T)$ plots for BA ($i = 1$) and ST ($i = 2$) copolymerization. It is evident that $\ln r_1$ is highly correlated with temperature, whereas $\ln r_2$ depends only slightly on temperature, which implies a very small difference between activation energies of the appropriate homo- and cross-propagation reactions.

The experimental results presented in *Figure 4* can be described by the following expressions (obtained by the least-squares method):

$$\ln r_1 = 1.3510 - 1034.1/T \text{ (correlation coefficient } -0.996) \qquad (16)$$

and

$$\ln r_2 = 0.05919 - 131.6/T \text{ (correlation coefficient } -0.806) \qquad (17)$$

where T is absolute temperature. This indicates that the appropriate values of activation energy differences between homo- and cross-propagation are $\Delta E_1 = 8.6\,\text{kJ mol}^{-1}$, and $\Delta E_2 = 1.1\,\text{kJ mol}^{-1}$.

Because there is now some evidence that partitioning of monomers between propagating polymer radicals and solvent (such partitioning could be affected by temperature) can be an important factor in copolymerization[15], one could argue that the difference in temperature sensitivity of reactivity ratios is only apparent. However, our studies were conducted in bulk, using pure monomers without any additives, so this excludes any influence of solvent on copolymerization. Moreover, Kaszas *et al.*[4], who carried out careful studies of BA–ST copolymerization at 50°C in bulk and in benzene solution, found that the values of reactivity ratios do not change with dilution by the solvent. Thus, our results should also be applicable to solution copolymerization in non-polar solvents. The solvent–polymer monomers partitioning can have some effect in highly polar solvents and should be elucidated before any application of our results to such solutions.

The question also arises whether, and to what extent, composition of BA–ST copolymers could be affected by the possible decomposition of ester groups at elevated temperatures. Grassie and Speakman[16], who investigated

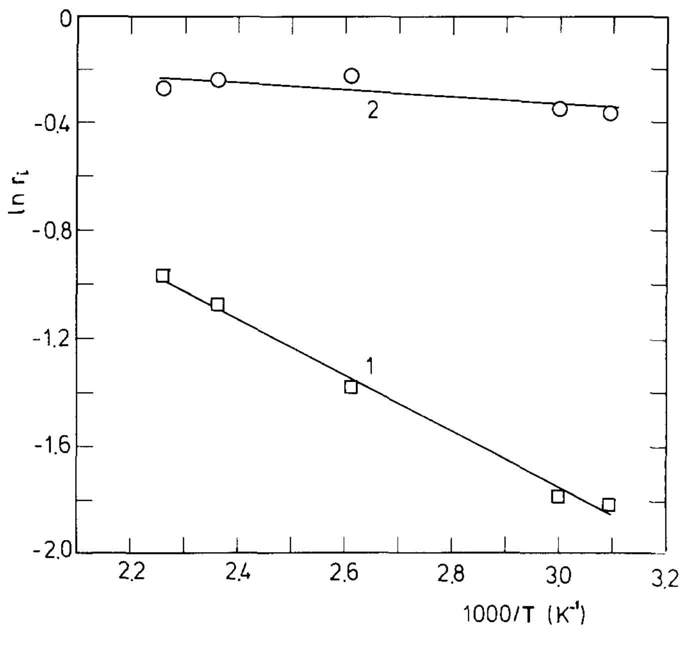

Figure 4 Arrhenius plot for temperature dependence of the reactivity ratios in the copolymerization of: 1 (□), butyl acrylate; 2 (○), styrene

thermal decomposition of various acrylates, found that although secondary esters are less stable, primary esters decompose only at high temperatures starting at 290–300°C. It should be noted that our studies were conducted for carefully degassed monomers at temperatures up to 170°C, therefore decomposition of ester groups should not have any significant effect on composition of our copolymers. Grassie and Speakman's[16] studies indicate that our results could be applicable to temperatures above 200°C. Although it is not possible in practice to reach the temperature at which BA–ST reactivity ratios become equal ($T=425$°C for $r_1=r_2$), still by selecting a suitably high polymerization temperature in the range up to 280–290°C it is possible to diminish the difference between the reactivity ratios, and thus reduce the copolymer compositional distribution for a simple batch process, or lessen the difference between copolymer and residual comonomer compositions if the process is continuous. Recently, values of reactivity ratios predicted on the basis of Arrhenius equations developed in this work were shown to properly describe relationships between copolymer and unreacted comonomer compositions for a continuous BA–ST copolymerization at temperatures above 200°C[17].

In conclusion, it seems to be reasonable to expect that our findings could be applicable to the primary alkyl acrylates–ST copolymerization even at temperatures above 200°C provided the process is conducted in an oxygen-free non-polar environment.

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