Thermal styrene/butyl acrylate co-oligomerization in a continuous stirred tank reactor

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Styrene (ST)/butyl acrylate (BA) copolymers with average molecular weights as low as $\bar{M}_n = 1500$ and $\bar{M}_w = 3000$, i.e. co-oligomers, were synthesized thermally at 230–280°C in a continuous stirred tank reactor without any added chain transfer agent. The products were characterized by size exclusion chromatography in conjunction with multiwavelength u.v., as well as by i.r., ^{1}H n.m.r. and differential scanning calorimetry. The molecular weights of the products decreased with increasing BA content in the monomer feed. The relationship between the residual monomer composition and the product composition can be modelled satisfactorily using a mathematical model based on the instantaneous copolymerization equation and Arrhenius relationships for the reactivity ratios. The devolatilized products varied in form from elastic semisolids through glue-like liquids to viscous liquids.

(Keywords: copolymerization; co-oligomerization; thermal polymerization)

INTRODUCTION

Styrene (ST)/butyl acrylate (BA) low molecular weight (MW) copolymers, i.e. co-oligomers, can be useful as plasticizers, adhesives and so on. The simplest way to produce neat ST/BA co-oligomers might be a thermal bulk process devoid of catalysts, chain transfer agents or other additives. In a recent article[1] we showed that the difference between the BA and ST reactivity ratios decreases with temperature increase. On the other hand, it is known that styrene can initiate free-radical polymerization at elevated temperatures[2–4], and that this thermal polymerization at temperatures above 200°C yields polymers with number-average molecular weights[5] below 50000. Thus, thermal copolymerization of styrene and butyl acrylate at high temperatures seems to be a promising way of producing ST/BA low MW copolymers.

The main purpose of the present work is to examine the possibility of synthesizing such ST/BA co-oligomers by a high temperature process and estimate the influence of reaction temperature and comonomer mixture composition on the properties of the products.

EXPERIMENTAL

Technical grade monomers were employed without further pretreatment. Styrene (inhibited with 10 ppm 4-t-butylcatechol) was obtained from Aldrich (Milwaukee, USA) and n-butyl acrylate (inhibited with 50 ppm monomethyl ether of hydroquinone) from Rohm and Haas (West Hill, Canada).

Syntheses were carried out thermally, i.e. without addition of any free-radical initiator.

In preliminary high temperature batch experiments, 7 mm (outer diameter) ampoules (degassed twice at 10^{-4} mmHg before sealing) were used.

A continuous stirred tank reactor (CSTR) of the same design as described by Hamielec and coworkers[6,7] was used, but the inner core was changed to give a lower reactor volume (400 ml). The syntheses were carried out after degassing the monomer feed and purging it with nitrogen. For all the runs, a pressure of ca. 3.5 MPa was maintained. The CSTR was followed by a flash devolatilizer. A general description of the reaction conditions and product yields is given in *Table 1*.

The product composition was determined by means of i.r. spectroscopy (using the carbonyl band at 1730 cm^{-1} as described previously[1]). In selected cases the composition data were verified by ^{1}H n.m.r. at 500 MHz.

Size exclusion chromatography (s.e.c.) analyses were performed using a system made up of four Styragel (Waters) columns. This system consisted of a train of μStyragel 10^4, Ultrastyragel 10^3, μStyragel 500 and Ultrastyragel 100 Å columns eluted with THF (1 ml min^{-1}). The system was calibrated using a series of TSK standards of linear polystyrene (Toyo Soda, supplied by Varian). A Hewlett–Packard 1040A multiwavelength (200–600 nm) u.v. spectrophotometer was used as the detector; u.v. spectra of the eluate were taken every 3.48 s and stored in computer memory.

Glass transition temperatures were measured with a Du Pont 910 differential scanning calorimeter at a 20°C min^{-1} heating rate.

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Table 1 Reaction conditions for ST/BA thermal co-oligomerizations in a CSTR

Run	Monomer feed ST/BA (mol%)	Temperature (°C)	Mean residence time (min)	Produce yield (wt%)
5R23	100/0	230	41	65.9
5R26	100/0	260	41	78.2
5R28	100/0	280	41	82.5
4R23	75/25	230	40	66.1
4R26	75/25	260	40	80.3
4R28	75/25	280	40	84.6
3R23	50/50	230	41	60.4
3R26	50/50	260	41	76.4
3R28	50/50	280	41	85.6
2R23	33/67	230	41	59.0
2R26	33/67	260	40	72.1
2R28	33/67	280	40	81.3
R23	25/75	230	41	57.0
R26	25/75	265	42	77.2
R28	25/75	280	42	82.1

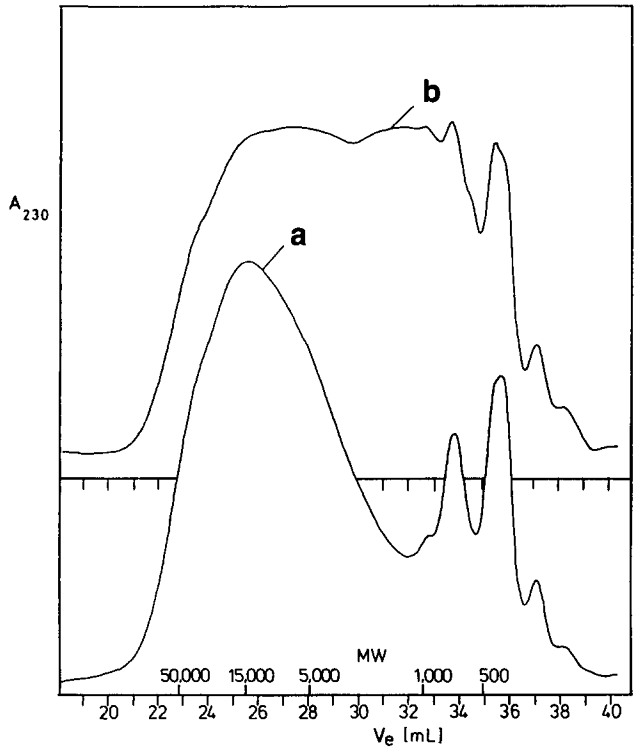

Figure 1 S.e.c. chromatograms (absorbance at 230 nm *versus* elution volume) for ST/BA co-oligomerization products from a high temperature batch process (monomer composition ST/BA of 50/50 mol%, temperature 230°C) after two reaction times: (a) 5 min, product composition ST/BA of 56/44 mol%; (b) 45 min, product composition ST/BA of 51/49 mol%

RESULTS AND DISCUSSION

Initially, in order to check the feasibility of ST/BA co-oligomer production by a simple high temperature batch process, we polymerized an equimolar ST/BA mixture in ampoules at 230 and 250°C. Despite the high temperatures employed where the difference between the reactivity ratios is greatly reduced[1], the resultant products still differed significantly from each other in molecular weight distribution and copolymer composition as a function of reaction time (*Figure 1*).

Consequently, we used a continuous stirred tank reactor (CSTR) at high temperatures. This attempt was successful. The bulk process was controllable and, despite high conversions, the products obtained had relatively narrow molecular weight distributions and were compositionally quite uniform, as shown by size exclusion chromatography (s.e.c.) in conjunction with u.v. analysis. *Figure 2* shows a typical three-dimensional (absorbance–wavelength–elution volume) graph for such a product.

The copolymers were synthesized for a wide range of monomer feed compositions (ST/BA from 100/0 to 25/75 mol%) at temperatures in the range 230–280°C (*Table 1*). Product yields depended on temperature and varied from 57–66 wt% at 230°C to 72–80 wt% at 260°C and 81–85 wt% at 280°C.

Figures 3–5 illustrate the relationships between the synthesis parameters and molecular weight distributions (MWDs) of the products. *Figures 3* and *4* show the influence of monomer feed composition on the MWDs of products synthesized at constant temperatures of 280 (*Figure 3*) and 260°C (*Figure 4*). *Figure 5* demonstrates the effect of temperature on the MWD of the product obtained at a constant (50/50 mol%) monomer feed composition.

It is evident from the s.e.c. traces that in the course of thermal ST/BA copolymerization the lowest oligomers (MW < 500) are generated in much greater quantities than might be expected from the normal distribution of molecular weights. On the other hand, it is known[2–4,8] that heating of styrene monomer leads to the formation of unstable cyclic dimers by a Diels–Alder reaction. These intermediates (stereoisomers of 1,2,3,8a-tetrahydro-1-phenylnaphthalene) can undergo secondary reactions leading to radicals or stable cyclic low oligomers, mostly trimers. Our present results for high temperature continuous ST homopolymerization show that the products contain high amounts of cyclic oligomers with MW < 500, mainly ST trimers (*Figures 3a* and *4a*). However, from our other s.e.c. results presented in *Figures 3–5* it is obvious that although by heating ST/BA mixtures we were also able to generate significant amounts of low oligomers, the oligomers produced in the

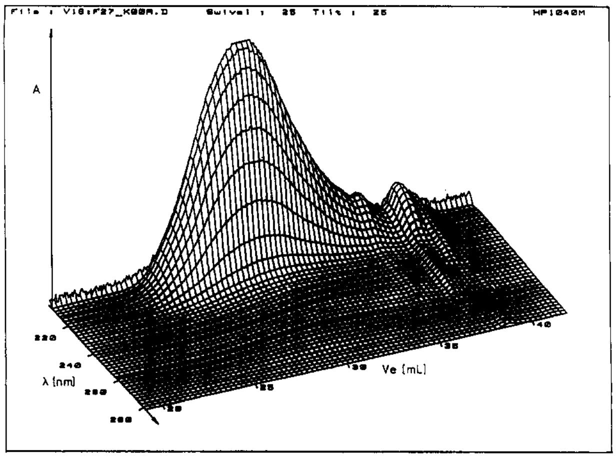

Figure 2 A typical s.e.c.–multiwavelength u.v. chromatogram (absorbance–wavelength–elution volume) for an ST/BA co-oligomerization product (2R26) obtained in a CSTR at high temperature

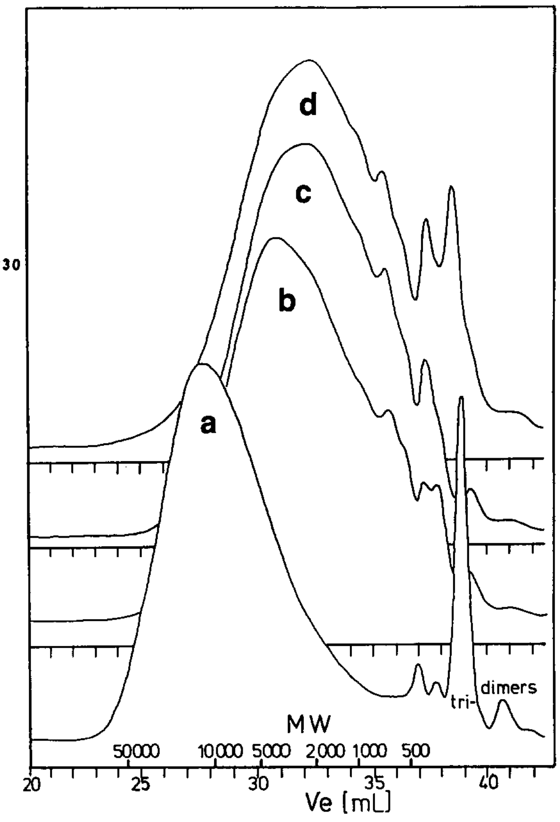

Figure 3 S.e.c. chromatograms (absorbance at 230 nm *versus* elution volume) for ST/BA co-oligomers synthesized in the CSTR, showing the influence of monomer feed composition (ST/BA ratio) on the MWD of the product synthesized at 280°C: (a) 100/0 mol%; (b) 50/50 mol%; (c) 33/67 mol%; (d) 25/75 mol%

most extensive amounts cannot be ST homotrimers since they have different s.e.c. elution volumes. Nevertheless, such oligomers can be ST/BA cyclic adducts, which naturally should have different hydrodynamic volumes from the corresponding ST oligomers.

It has been demonstrated[9,10] that in the thermal copolymerization of ST with acrylonitrile (AN) the initial step is analogous to the thermal polymerization of pure styrene, i.e. a Diels–Alder reaction takes place. However, no ST homotrimers but various ST/AN cotrimers were found instead in the copolymerization products. This happened because AN is more dienophilic than ST and in the Diels–Alder reaction acts as the dienophile instead of another ST molecule.

Since acrylates are also more dienophilic than ST, it is highly probable that the mechanism of the formation of cyclic ST/BA co-oligomers is analogous to the mechanism in the ST/AN system. Thus, initially, cyclic ST/BA adducts are formed by a Diels–Alder reaction. These intermediates react further with ST or BA to form various cyclic low co-oligomers and/or monoradicals which initiate the growth of linear copolymers. Stable cyclic ST/BA co-oligomers can also result from combination of these radicals and/or radicals formed by a transfer reaction. Consequently, we assumed that the lowest oligomers (dimers, trimers and tetramers) were of cyclic structure and were formed predominantly by non-chain reactions. This hypothesis is supported by the results of u.v. analysis in conjunction with s.e.c., which indicate that the lowest oligomers have u.v. spectra different from the rest of the product (*Figure 2*).

Hence, to estimate the molecular weights of the products formed by a linear free-radical ST/BA addition we calculated $\bar{M}_w$ and $\bar{M}_n$ on the basis of the s.e.c. chromatograms taking into account species up to the elution volume $V_e = 36.5$ ml. The results of these average molecular weight estimations, as well as the molecular weights corresponding to the s.e.c. peaks, are presented in *Table 2*. Please note that owing to an s.e.c. resolution inadequacy for low MWs the peaks for cyclic and linear co-oligomers could not be completely resolved. Nevertheless, on the basis of the s.e.c. chromatograms and the results of the average molecular weight estimations we can draw the following conclusions.

1. The molecular weights of the products obtained by a free-radical linear addition depend, as expected, on the reaction temperature for a given monomer feed composition, i.e. the higher the temperature of synthesis, the lower the molecular weights of the products.
2. The molecular weights of these products also depend clearly on the ST/BA ratio at a given reaction temperature, i.e. the higher the BA content in the comonomer feed, the lower the molecular weights of the products synthesized under the same conditions.

It has already been shown[11] that chain transfer to low MW species plays an important role in controlling the molecular weights during the ST polymerization. Studies by Olaj *et al.*[3] have revealed that transfer to Diels–Alder intermediates having double-allylic hydrogen atoms is

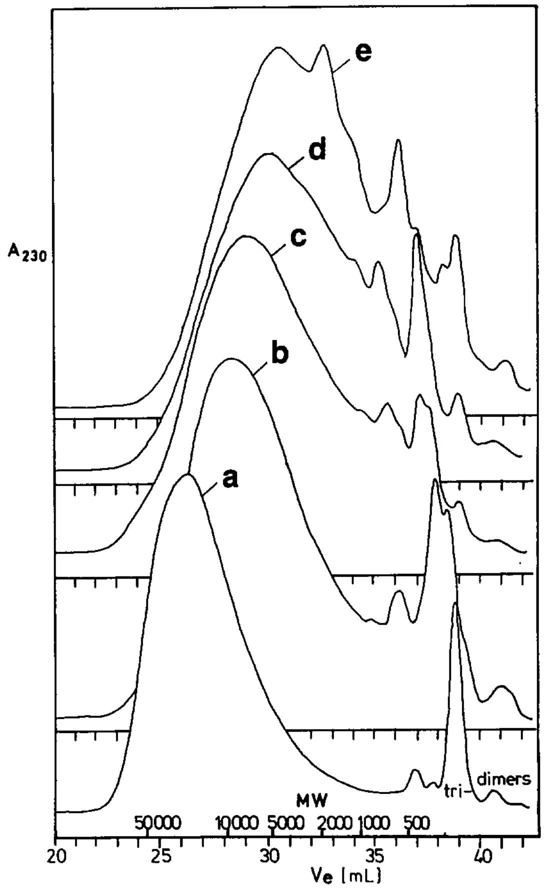

Figure 4 S.e.c. chromatograms (absorbance at 230 nm *versus* elution volume) for ST/BA co-oligomers synthesized in the CSTR, showing the influence of monomer feed composition (ST/BA ratio) on the MWD of the product synthesized at 260°C: (a) 100/0 mol%; (b) 75/25 mol%; (c) 50/50 mol%; (d) 33/67 mol%; (e) 25/75 mol%

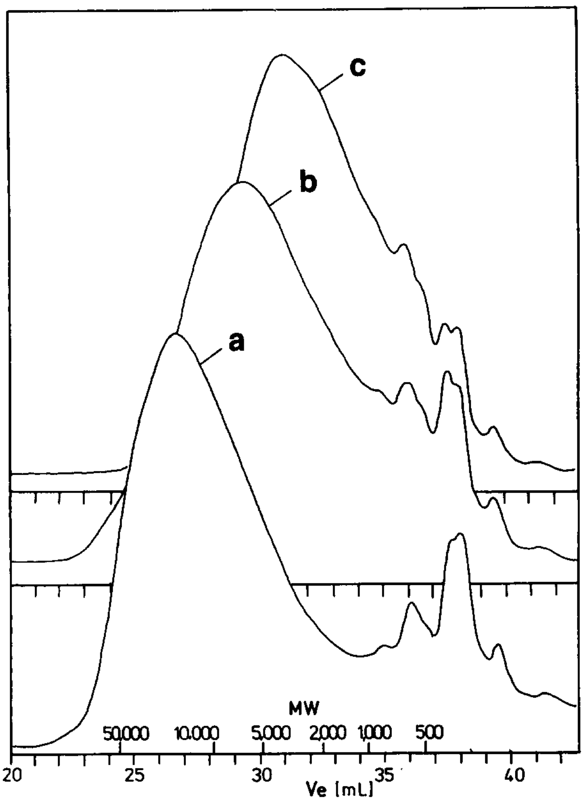

Figure 5 S.e.c. chromatograms (absorbance at 230 nm *versus* elution volume) for ST/BA co-oligomers synthesized in the CSTR, showing the influence of reaction temperature on the MWD of the product obtained using a 50/50 mol% monomer feed at: (a) 230°C; (b) 260°C; (c) 280°C

Table 2 Molecular weights of ST/BA co-oligomerization products synthesized in a CSTR

Run	Average molecular weights		
	$\bar{M}_n$	$\bar{M}_{peak}$[a]	$\bar{M}_w$
5R23	16 600	57 900	52 900
5R26	7 400	19 000	23 350
5R28	4 400	9 600	12 400
4R23	3 000	9 300	12 300
4R26	2 800	7 000	10 300
3R23	3 700	14 500	17 550
3R26	2 300	4 500	8 700
3R28	1 700	2 800	3 750
2R26	1 900	3 150	5 700
2R28	1 500	1 900	3 050
R26	1 600	1 500	4 300
R28	1 500	1 800	3 300

[a] Molecular weight corresponding to the main s.e.c. peak

unusually high: the axial stereoisomer of 1,2,3,8a-tetrahydro-1-phenylnaphthalene has a chain transfer constant of ca. 100 at 80°C, which is higher than in the case of mercaptans. Products of the Diels–Alder reaction between ST and BA should also have double-allylic hydrogen atoms. An increase in the content of dienophilic BA in the monomer feed should increase the ST/BA Diels–Alder adduct concentration during our continuous process, and thus facilitate chain transfer reactions. This hypothesis is supported by our findings that an increase in BA content raises the amount of cyclic low ST/BA oligomers at any given temperature.

The molecular weight distribution of the linear polymer product from a CSTR can be calculated from the instantaneous polymerization degree (r) distribution

$$W(r)=(\tau+\beta)[\tau+(\beta/2)(\tau+\beta)(r-1)]r\Phi^{r+1} \quad (1)$$

with the dimensionless parameters τ and β given by

$$\tau=(R_f+R_{td})/R_p$$

$$\beta=R_{tc}/R_p$$

and

$$\Phi=1/(1+\tau+\beta)$$

where R_p is the propagation rate $(=k_p[R\cdot][M])$, R_f is the overall chain transfer rate $(=\{\Sigma k_{fT_i}[T_i]\}[R\cdot])$, R_{td} is the rate of termination by disproportionation and R_{tc} is the rate of termination by combination. Since $W(r)\mathrm{d}r=W(\mathrm{MW})\mathrm{dMW}$ and $\mathrm{dMW}/\mathrm{d}r=M$ (where M is the effective monomer molecular weight), we can write $W(\mathrm{MW})=W(r)/M$.

To verify how important is chain transfer to the Diels–Alder intermediates in controlling the molecular weights at high temperatures, we calculated the MWD for the ST high temperature polymerization by applying equation (1) and assuming that the effect of termination reactions on the MWD can be neglected. Individual concentrations of the Diels–Alder adducts and their chain transfer constants were estimated by using the data of Olaj *et al.*[3] for various temperatures and assuming Arrhenius-type relationships. The MWDs predicted in this way for ST polymerizations at temperatures in the range 230–280°C are presented in *Figure 6*. For 230 and 260°C, the estimation, which assumed that chain transfer to the Diels–Alder intermediates is solely responsible for controlling the MWs, gives values which are only slightly higher than the MWs observed in the present work. For 280°C the predicted MWs are more significantly higher than actually observed. However, it is known[12] that when polystyrene is heated at temperatures around 300°C chain scission occurs at a measurable rate, while volatile production remains negligible. Thus it is possible that at 280°C random scission of linear chains has already a significant effect on polystyrene molecular weights and leads to their further decrease.

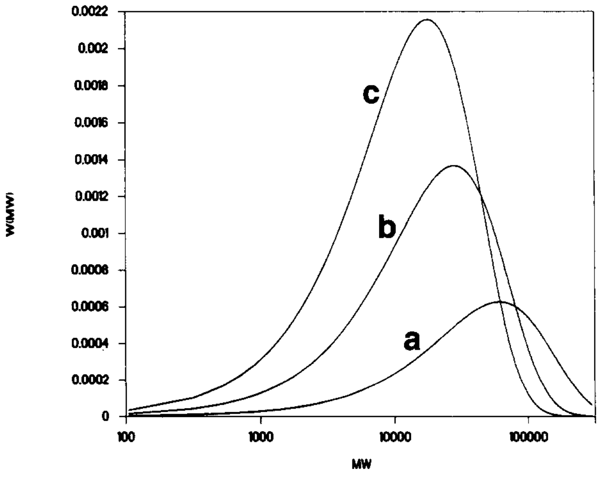

Figure 6 ST homopolymer molecular weight distributions calculated according to equation (1) for the following temperatures: (a) 230°C; (b) 260°C; (c) 280°C

Table 3 Average compositions of products from ST/BA co-oligomerizations in a CSTR[a]

Monomer feed composition (molar fraction of BA)	Temperature (°C)	Product composition (molar fraction of BA units)
0.250	230	0.240
0.250	260	0.245
0.250	280	0.251
0.500	230	0.493
0.500	260	0.486
0.500	280	0.497
0.667	230	0.616
0.667	260	0.641
0.667	280	0.654
0.750	230	0.700
0.750	265	0.729
0.750	280	0.737

[a] Nominal residence time 40 min

A similar calculation of the MWD might be performed for ST/BA copolymerization by using the concept of pseudo-rate constants[13]. There are, however, no data on the chain transfer constants and the concentrations of ST/BA Diels–Alder intermediates. Our preliminary calculations, which assumed that the chain transfer constants for ST/BA codimers are equal to those for ST dimers, predicted molecular weights which are distinctly higher than observed. Some possible reasons for this discrepancy are as follows: (1) ST/BA adducts could actually be more reactive in chain transfer than ST dimers (a different kind of steric hindrance); (2) the stationary concentrations of the ST/BA adducts could be much higher than for ST dimers owing to the faster Diels–Alder reaction; (3) there could be a significant influence of penultimate effects for short chains; and (4) random scission of ST/BA copolymer chains at high temperatures could also have some impact on the MWs of ST/BA high temperature copolymerization products. (From the studies of Grassie and Speakman[14] concerning degradation of polyacrylates, it can be inferred that some chain scission occurs also at temperatures around 280°C. Zislina *et al.*[15], who studied degradation of BA/ST copolymers at 300°C, found that incorporation of ST units into BA polymer chains seemed to enhance the chain scission in comparison to poly(BA).) All these effects should be addressed in a further modelling of the molecular weight distributions of ST/BA copolymerization products at high temperatures.

The compositions of the products after the removal of unreacted monomers are reported in *Table 3*. It is evident that in almost every case the content of BA units in the product is lower than the BA content in the appropriate monomer feed. Nevertheless, for a given monomer feed composition there is an increase in the content of BA units in the co-oligomer with increasing reaction temperature. This seems to be in qualitative agreement with the phenomenon of decreasing difference between ST and BA reactivity ratios with temperature increase described in our previous article[1]. However, this reasoning can be misleading because in a well-mixed CSTR in a steady state, the copolymer composition is governed by the monomer ratio in the mixture of residual unreacted monomers, not in the monomer feed.

Knowing the monomer feed composition as well as the average composition and overall yield of devolatilized product, we can find the composition of residual monomers. Let us consider numbers of moles of monomer molecules (or monomer units) entering and leaving the steady-state CSTR within any time unit

$$W_{\text{in}}/(f_{1,\text{in}}M_1 + f_{2,\text{in}}M_2) = W_{\text{rm}}/(f_1M_1 + f_2M_2) + W_{\text{pr}}/(F_1M_1 + F_2M_2) \quad (2)$$

where W_{in}, W_{rm} and W_{pr} are the weight flow rates of the monomer feed, residual monomers and product (after removal of residual monomers), respectively; $f_{1,\text{in}}$, f_1 and F_1 are the corresponding BA molar fractions; $f_{2,\text{in}}$, f_2 and F_2 are the ST molar fractions; and M_1 and M_2 are the molecular weights of BA and ST, respectively. The foregoing equation can also be expressed as

$$1/[M_2 + f_{1,\text{in}}(M_1 - M_2)] = C_{\text{w}}/[M_2 + F_1(M_1 - M_2)] + (1 - C_{\text{w}})/[M_2 + f_1(M_1 - M_2)] \quad (3)$$

where C_{w} is the overall weight conversion. With a little algebra one obtains the expression to find the composition of residual monomers

$$f_1 = \{(C_{\text{w}} - 1)/[C_{\text{w}}/(M_2 + F_1\Delta M) - 1/(M_2 + f_{1,\text{in}}\Delta M)] - M_2\}/\Delta M \quad (4)$$

where $\Delta M = M_1 - M_2$.

In investigating thermal bulk BA/ST copolymerization, we had previously found[1] that the temperature dependences of the reactivity ratios can be described by the following Arrhenius expressions

$$\ln r_{\text{BA}} = 1.3510 - 1034.1/T \quad (5)$$

$$\ln r_{\text{st}} = 0.05919 - 131.6/T \quad (6)$$

where T is the absolute temperature. Using these equations for the appropriate temperatures, we estimated the reactivity ratios in the present studies. Then we predicted the relationship between the residual monomer composition f_1 and the copolymerization product composition F_1 by substituting these values into the following mathematical model based on the instantaneous copolymerization equation

$$[f_1 + (r_{\text{BA}} - 1)f_1^2]/[r_{\text{ST}} + 2(1 - r_{\text{ST}})f_1 + (r_{\text{BA}} + r_{\text{ST}} - 2)f_1^2] - F_1 = 0 \quad (7)$$

The results of the modelling for temperatures in the range 230–280°C, together with our experimental results, are presented in *Figure 7*.

In general, there is good agreement between the values predicted on the basis of this model and the experimental results. However, it should be noted that at 230 and 260°C the model predicts in almost every case F_1 values slightly higher than those found experimentally. This can be explained as follows.

1. In the case of relatively low MW copolymer chain production, the terminal model cannot be strictly obeyed because penultimate effects and the chain length dependence of the rate constants should be more important than for typical copolymerization conditions.
2. The presence of cyclic low oligomers produced by non-chain reactions can blur the results of copolymer-

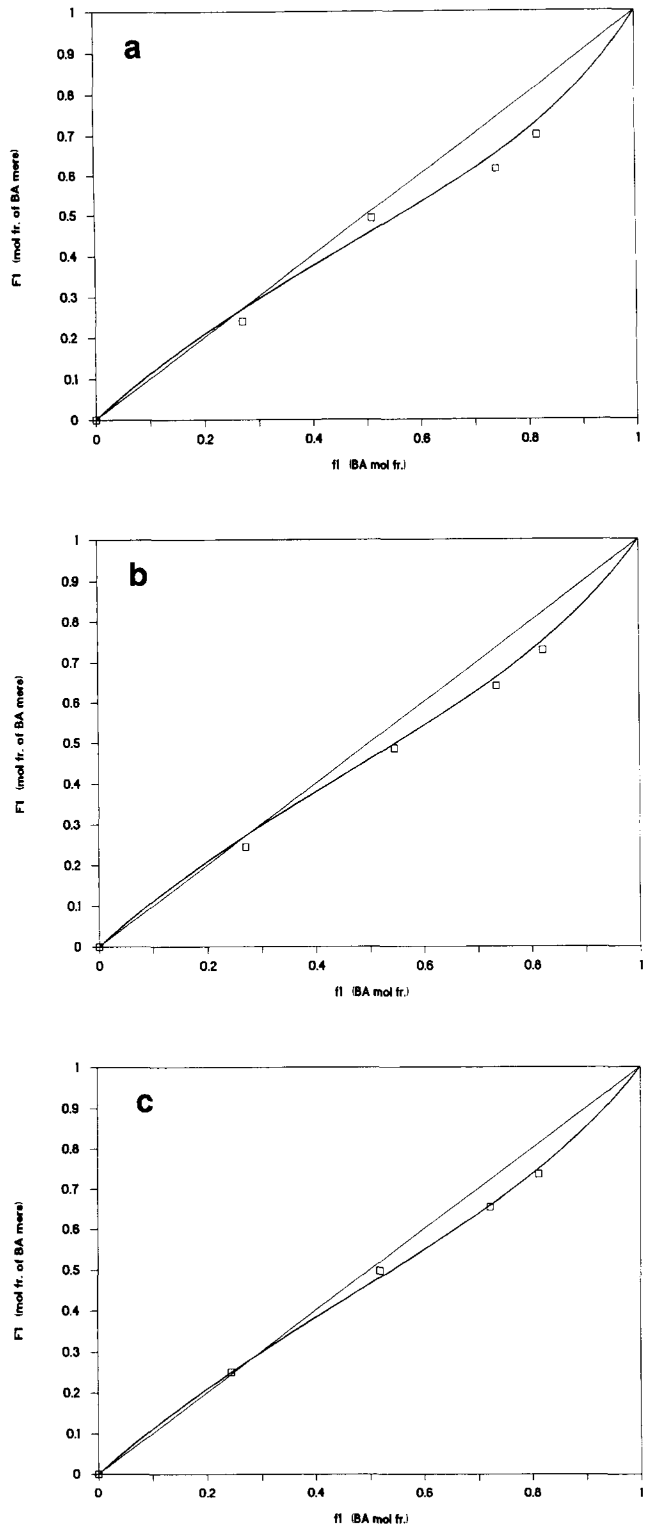

Figure 7 Copolymer composition F_1 *versus* residual comonomer composition f_1 for BA/ST copolymerization at: (a) 230°C; (b) 260°C; (c) 280°C. The curves were calculated using the mathematical model (equation (7)) with reactivity ratios estimated according to equations (5) and (6). The symbols (□) represent the CSTR experimental results

ization product composition determination. (This effect can, however, be of minor importance when these cyclic oligomers have an average composition not much different from the composition of the linear co-oligomers; this is possible only in the case of ST/BA adducts.)

The question also arises as to what extent the composition of BA/ST copolymers could be affected by the possible decomposition of ester groups at high temperatures. Grassie and Speakman[14], who investigated thermal decomposition of various polyacrylates, found that although polymers of secondary esters are less stable, polymers of primary esters decompose only at high temperatures starting at 300°C. In fact, their results for a two hour degradation of poly(BA) at various temperatures indicate that at 280°C no measurable amounts of volatiles should be evolved. Moreover, Zislina *et al.*[15], who studied degradation of BA/ST copolymers at 300°C under vacuum, found that incorporation of ST units into BA polymer chains has some inhibiting effect on evolution of volatiles.

Under the conditions investigated by us, the limitations discussed above seem to play an insignificant role. The simple instantaneous copolymerization equation with parameters predicted according to Arrhenius expressions is still satisfactory in modelling the relationship between the composition of unreacted monomers and the composition of ST/BA copolymerization products synthesized in a CSTR at temperatures up to 280°C.

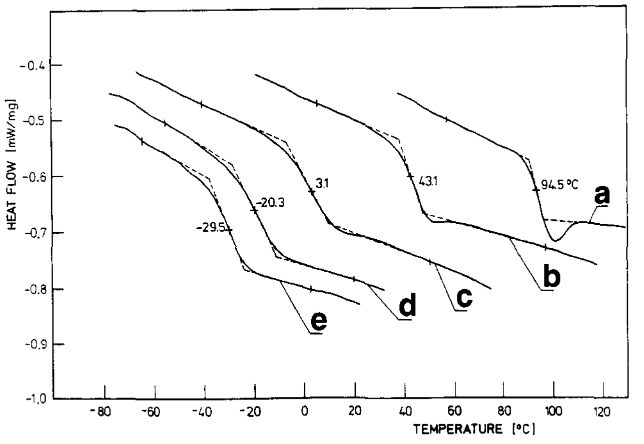

Figure 8 Differential scanning calorimetry thermograms (heating rate 20°C min^{-1}) illustrating the influence of monomer feed composition on the glass transition temperatures of ST/BA co-oligomers synthesized in a CSTR (at 260°C) using various monomer feed compositions (ST/BA ratios): (a) 100/0 mol%; (b) 75/25 mol%; (c) 50/50 mol% (d) 33/67 mol%; (e) 25/75 mol%

Table 4 Glass transition temperatures for ST/BA co-oligomerization products synthesized in a CSTR

	Glass transition temperature (°C)		
Sample	Onset	Midpoint	End
5R23	99.3	101.4	104.0
5R26	91.5	94.5	97.6
5R28	85.0	87.6	90.7
4R23	89.0	97.2	105.7
4R26	38.1	43.1	48.3
3R23	−4.5	6.2	16.8
3R26	−6.9	3.1	9.9
3R28	−17.2	−8.4	0.4
2R26	−29.4	−20.3	−12.3
2R28	−38.1	−28.6	−20.2
R26	−37.3	−29.5	−23.7
R28	−44.2	−37.0	−29.7

Since the co-oligomers produced might be useful in practice as plasticizers or adhesives, it was of interest to examine their glass transition temperatures.

The glass transition temperatures of these devolatilized products depend not only on their molecular weights but also on the content of BA units (*Table 4*). *Figure 8* shows that at a given reaction temperature (260°C) it is possible to control the glass transition temperature of the product by changing the monomer feed composition.

It is interesting that some products are liquid at room temperature. This applies to the case of co-oligomers containing 50 mol% or more of BA oligomers and having molecular weights ($\bar{M}_{\text{peak}}$) below 3200. These co-oligomers show glass transition temperatures (the midpoint) in the range −37 to −8°C and can be used as non-volatile plasticizers. Some other ST/BA co-oligomerization products are glue-like liquids and might be useful as adhesives.

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