

## CHARACTERISTIC EVENTS IN FREE RADICAL POLYMERIZATION OF LOWER *n*-ALKYL METHACRYLATES

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### Abstract

It is well known that the free radical bulk polymerization of lower *n*-alkyl methacrylates is characterized by autoacceleration after definite conversions of the monomers. The conversion vs. time curves of polymerization have a typical 'S' shape. There are several characteristic points in these curves: the onset of autoacceleration (point M), the maximum in the polymerization rate (point S) and the end of the polymerization (point K). We have observed points P and R (maximum and minimum of autoacceleration) as inflection points in the derived polymerization rate vs. time curve.

In this work, the free radical bulk polymerizations of methyl, ethyl and butyl methacrylates were investigated by differential scanning calorimetry. The effects of the polymerization temperature and the alkyl group length in the esters on the monomer conversions at the points M, P, S, R and K were studied. By regression analysis of the experimental results, relations were developed with which it is possible to predict the positions of the characteristic points, depending on the polymerization temperature and the alkyl group length.

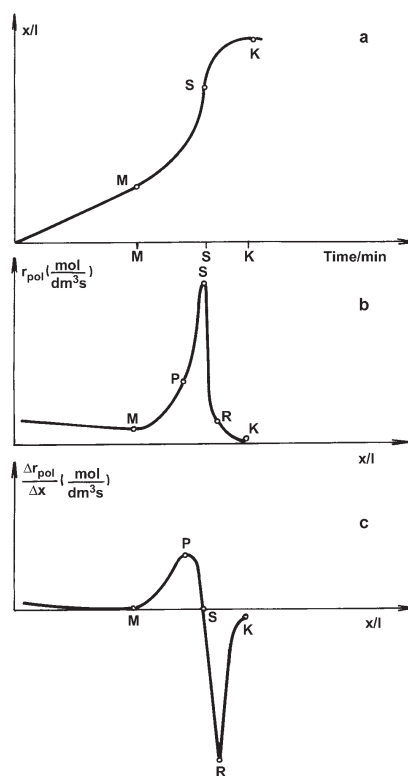
**Keywords:** *n*-alkyl methacrylates, autoacceleration, characteristic events, polymerization

### Introduction

The free radical polymerizations of *n*-alkyl methacrylates, and especially that of methyl methacrylate, have been frequently investigated because of the very pronounced autoacceleration phenomenon known as the gel effect or the Norrish-Trommsdorf effect [1–4]. A number of studies of methyl methacrylate polymerization have been published, and many models have been developed with a view to explaining the onset of the gel effect [1, 5–11]. The gel effect phenomenon in the polymerization of some alkyl methacrylates has been observed by many other investigators too [12–17].

The conversion vs. time curves of *n*-alkyl methacrylate polymerization have a typical 'S' shape. There are five characteristic points in these curves (Fig. 1a). Three of them have been investigated by many authors: the onset of autoacceleration (point M), the maximum in the polymerization rate (point S) and the end of the polymerization (point K). The onset of autoacceleration (Fig. 1, M) is the moment when the polymerization rate

departs from the value anticipated by the classical theory of free radical polymerization [18–21]. The minimum (M) in the polymerization rate vs. time curve (Fig. 1b) was first observed by Schulz [18]. The temperature, and the type and the concentration of the initiator are the factors determining the onset and the intensity of autoacceleration. The conversion at point M ( $X_m$ ) increases with increase of the initiator concentration [5, 18, 22, 23] and the polymerization temperature [5, 24–27]. In the presence of initiators with high decomposition rate constants, the onset of the gel effect was less pronounced [28].  $X_m$  increases with increase in the alkyl group length in the alkyl methacrylates [29–33].



**Fig. 1** General shapes of conversion (a), polymerization rate (b) and derived polymerization rate (c) curves during MMA polymerization (characteristic points: M, P, S, R and K are presented)

The final conversion,  $X_k$  (at point K, Fig. 1), is determined when the polymerization rate vs. time curve becomes horizontal and the rate of the polymerization becomes close to zero.  $X_k$  increases with the initiator concentration [19, 34–36], although there have been some results [26, 37, 38] where  $X_k$  was independent of the initiator concentration; it also increases with increase of the polymerization temperature [26, 36, 37, 39–41].  $X_k$  decreases with increase of the polymerization temperature when methyl methacrylate is polymerized at a temperature above the glass transition

temperature [42, 43]. It increases with increase in the alkyl group length in methacrylic acid ester [5, 16, 25, 29, 44].

Point S (an inflection in the conversion vs. time curve, Fig. 1a, i.e. a maximum in the polymerization rate curve, Fig. 1b) has not been especially investigated. The only exception is the paper by Schulz [18], who discovered that the conversion at point S ( $X_s$ ) is independent of the initiator concentration, but increases with the polymerization temperature.

We earlier observed the characteristic points P and R [23], the maximum and minimum in the autoacceleration, as inflection points in the derived polymerization rate vs. time curve (Fig. 1c).

In the current literature most of the published data are related to the examination of the propagation and termination kinetics in free radical polymerization of alkyl methacrylates [45–48]. There are some results about the investigation of characteristic events in free radical polymerization of methyl methacrylate [49, 50]. Experimental results presented by O'Neil *et al.* [49] were consistent with the quantitative trend predicted by free volume concept for the conversion at point M as a function of the polymerization temperature. A method for the selection of models for determination of the final conversion depending on the polymerization temperature exhibiting gel and glass effects has been developed [50].

The aim of the present work was a systematic study of the characteristic events in the polymerizations of methyl, ethyl, and butyl methacrylates. The effects of the polymerization temperature and the alkyl group length in the esters on the conversions at points M, P, S, R and K have been investigated. The free radical bulk polymerization of the above monomers were studied by differential scanning calorimetry (DSC).

## Experimental

### Chemicals

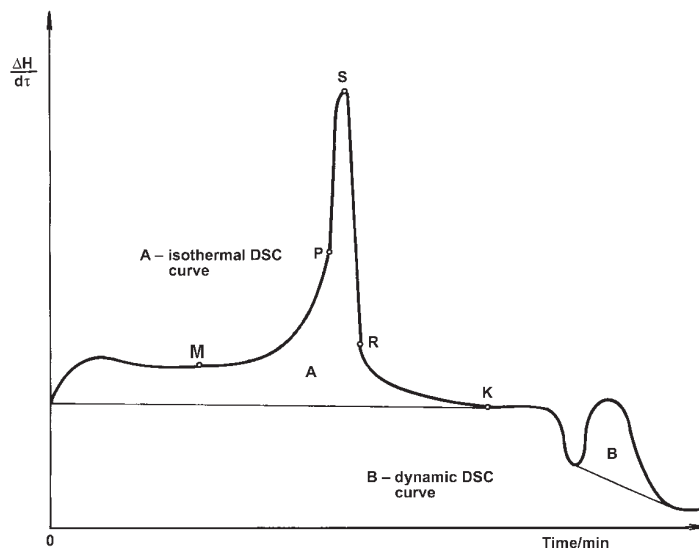
- Methyl methacrylate (MMA),  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$ , Merck.
- Ethyl methacrylate (EMA),  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$ , Merck.
- Butyl methacrylate (BMA),  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$ , Merck.

The monomers were freed of inhibitor and distilled under nitrogen and reduced pressure.

– Initiator: 2,2'-azobisisobutyronitrile (AIBN), p.a., Merck, was recrystallized from methanol.

### Methods

The bulk polymerizations of MMA, EMA and BMA were studied by DSC, with a DuPont Model 910 instrument. The polymerizations were carried out under isothermal conditions in the temperature range 60–90 for MMA, 70–90 for EMA and



**Fig. 2** Typical DSC curves of polymerization of lower *n*-alkyl methacrylates: A – isothermal conditions of polymerization; B – dynamic thermal range (from temperature of isothermal polymerization up to 220°C)

75–90°C for BMA. The initiator concentration was 1 mass%. A typical DSC curve is presented in Fig. 2.

The heats evolved in the reaction (proportional to the amount of polymerized monomer) were calculated from the areas between the DSC curve and the baseline (Fig. 2, A), which was obtained by back-extrapolation of the horizontal straight line recorded after the polymerization was finished [29, 31]. The amount of unreacted monomer was determined by prolonging the polymerization in a dynamic thermal range (from the temperature of isothermal polymerization up to 220°C, Fig. 2, B).

Point M was determined as the minimum, and point S as the maximum in the DSC curve (Fig. 2, A). Point K was determined as the moment when the isothermal DSC curve became horizontal (Fig. 2, A). Point P was determined as the maximum, and point R as the minimum in the derived DSC curve (Fig. 1c). The reproducibility of the experimental data relating to the positions of the points M, P, S, R and K during MMA, EMA and BMA polymerization was in each case  $\pm 2\%$ .

The polymerization rates were calculated on the basis of the well-known relations from chemical kinetics, using the conversions of monomers determined from the DSC curves [32].

## Results and discussion

The free radical bulk polymerizations of MMA, EMA and BMA are characterized by a strong autoacceleration. The conversion vs. time curves have a typical ‘S’ shape

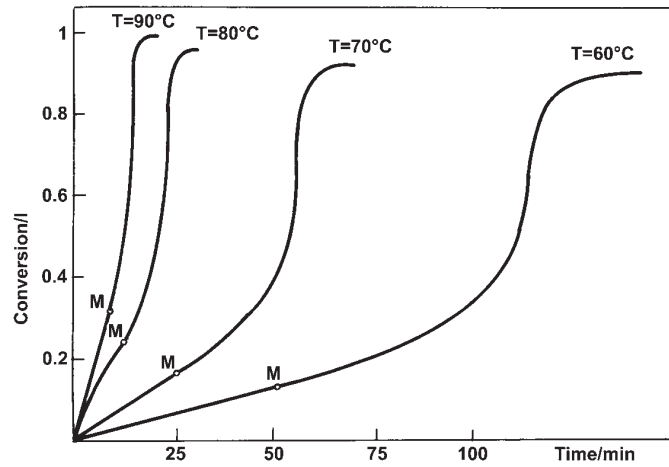


Fig. 3 Conversion vs. time curves of MMA polymerization (1 mass% AIBN)

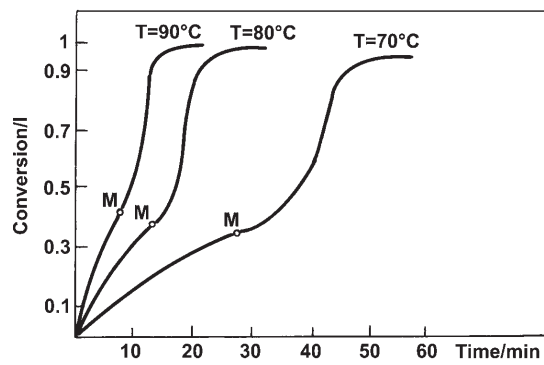


Fig. 4 Conversion vs. time curves of EMA polymerization (1 mass% AIBN)

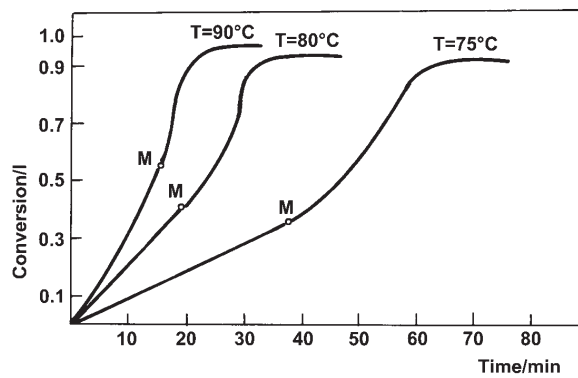
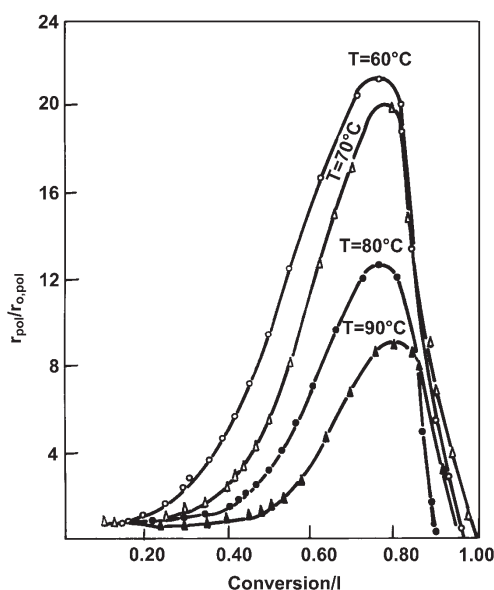


Fig. 5 Conversion vs. time curves of BMA polymerization (1 mass% AIBN)

(Figs 3–5) and the points M are clearly observed in them. The slopes of the conversion vs. time curves increase with increase of the polymerization temperature. The intensity of autoacceleration decreases with increase in the alkyl group length in the ester, since the slopes of the conversion vs. time curves of MMA polymerization are steeper than those of EMA and BMA polymerization (Figs 3–5). This is in agreement with the findings of other authors [5, 15, 29, 51].

According to Kargin and Kabanov [52], autoacceleration can be defined as  $r_{\text{pol}}/r_{0,\text{pol}}$ , where  $r_{\text{pol}}$  is the rate of polymerization at a defined moment of the reaction, and  $r_{0,\text{pol}}$  is the rate at the beginning of the reaction. The theory of the polymerization of organized monomers [52, 53] suggests that autoacceleration increases with increase of the monomer organization. The organization of monomers is known to decrease with increase of the temperature. Thus, it can be expected that autoacceleration decreases with increase of the polymerization temperature. The effects of the polymerization temperature on autoacceleration during MMA, EMA and BMA polymerizations are shown in Figs 6–8. Autoacceleration decreases with increase of the polymerization temperature. Our experimental data are in agreement with the concept of the polymerization of organized monomers.

It can be expected that the degree of organization of monomers will decrease with an increase in alkyl group length. Hence, according to Kargin and Kabanov [52] the autoacceleration will decrease too. Our results confirm this prediction (Figs 6–8), since the degree of organization of MMA is higher than that of EMA and BMA, thus



**Fig. 6** Effect of polymerization temperature on autoacceleration during MMA polymerization (1 mass% AIBN)

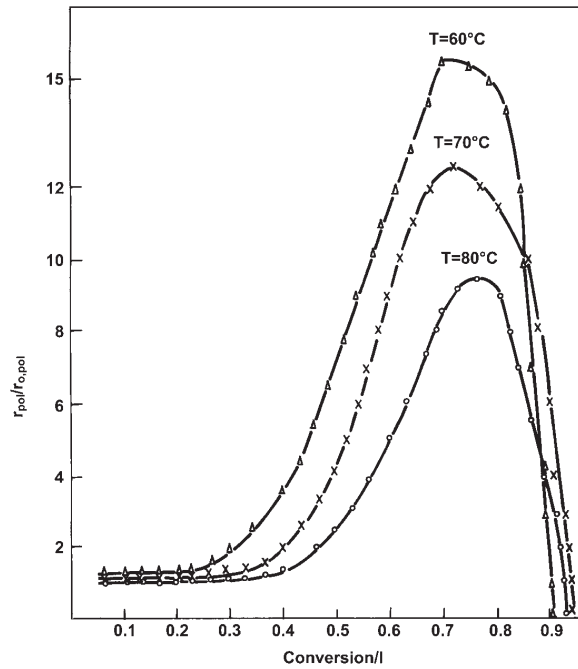


Fig. 7 Effect of polymerization temperature on autoacceleration during EMA polymerization (1 mass% AIBN)

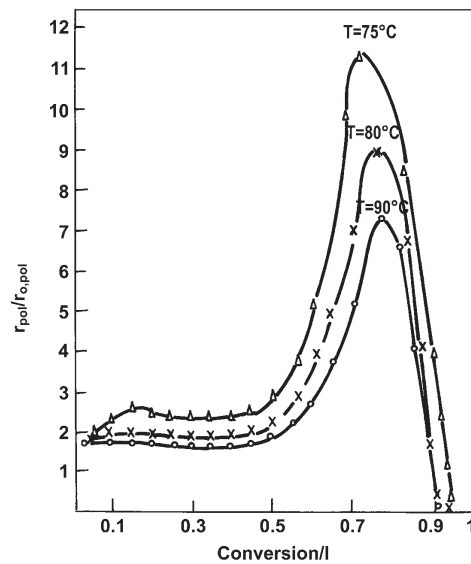


Fig. 8 Effect of polymerization temperature on autoacceleration during BMA polymerization (1 mass% AIBN)

autoacceleration is stronger expressed in MMA than in EMA and BMA polymerization.

The conversions at the characteristic points of MMA, EMA and BMA polymerization, as functions of the polymerization temperature and the alkyl group length, are given in Tables 1–4.

**Table 1** Effect of polymerization temperature on conversions at characteristic points of MMA polymerization (1 mass% AIBN)

| Conversion/<br>mass% | Polymerization temperature/°C |       |       |       |
|----------------------|-------------------------------|-------|-------|-------|
|                      | 60                            | 70    | 80    | 90    |
| $X_m$                | 12.21                         | 16.83 | 21.81 | 31.67 |
|                      | 13.78                         | 15.70 | 24.48 | 32.25 |
|                      | –                             | 13.20 | 24.93 | 31.56 |
| $X_p$                | 54.17                         | 60.63 | 62.90 | 65.83 |
|                      | 54.24                         | 59.43 | 64.24 | 65.02 |
|                      | –                             | 57.99 | 63.61 | 64.48 |
| $X_s$                | 74.58                         | 76.31 | 76.29 | 78.92 |
|                      | 72.80                         | 76.52 | 76.90 | 78.61 |
|                      | –                             | 75.60 | 76.56 | 78.89 |
| $X_r$                | 85.20                         | 89.90 | 92.55 | 96.97 |
|                      | 86.26                         | 89.14 | 93.59 | 97.12 |
|                      | –                             | 89.89 | 93.46 | –     |
| $X_k$                | 90.45                         | 92.64 | 95.44 | 99.04 |
|                      | 90.38                         | 92.81 | 95.48 | 99.13 |
|                      | –                             | 92.75 | 95.79 | 99.01 |

**Table 2** Effect of polymerization temperature on conversions at characteristic points of EMA polymerization (1 mass% AIBN)

| Conversion/<br>mass% | Polymerization temperature/°C |       |       |
|----------------------|-------------------------------|-------|-------|
|                      | 70                            | 80    | 90    |
| $X_m$                | 29.57                         | 36.70 | 38.96 |
|                      | 32.11                         | 36.66 | 38.63 |
|                      | 33.16                         | 35.11 | 40.01 |
| $X_p$                | 63.12                         | 67.79 | 69.03 |
|                      | 63.02                         | 66.63 | 68.33 |
|                      | 64.17                         | 66.93 | 69.21 |
| $X_s$                | 73.45                         | 74.32 | 78.44 |
|                      | 72.36                         | 74.95 | 77.98 |
|                      | 72.96                         | 75.37 | 78.92 |
| $X_r$                | 90.31                         | 93.92 | 94.49 |
|                      | 90.11                         | 92.61 | 94.56 |
|                      | 90.65                         | 92.93 | 95.12 |
| $X_k$                | 94.03                         | 98.05 | 99.17 |
|                      | 95.11                         | 97.32 | 98.73 |
|                      | 95.93                         | 97.01 | 99.07 |



**Table 3** Effect of polymerization temperature on conversions at characteristic points of BMA polymerization (1 mass% AIBN)

| Conversion/<br>mass% | Polymerization temperature/°C |       |       |
|----------------------|-------------------------------|-------|-------|
|                      | 75                            | 80    | 90    |
| $X_m$                | 34.00                         | 39.42 | 53.29 |
|                      | 34.93                         | 38.10 | 54.19 |
|                      | –                             | 39.17 | 53.17 |
| $X_p$                | 63.85                         | 65.11 | 72.91 |
|                      | 63.87                         | 65.17 | 71.87 |
|                      | –                             | 66.74 | 70.02 |
| $X_s$                | 69.79                         | 74.08 | 79.82 |
|                      | 68.11                         | 74.05 | 78.75 |
|                      | –                             | 73.87 | 77.88 |
| $X_r$                | 90.11                         | 91.85 | 92.99 |
|                      | 89.53                         | 92.05 | 92.24 |
|                      | –                             | 91.14 | 92.11 |
| $X_k$                | 93.66                         | 95.85 | 96.97 |
|                      | 92.66                         | 94.60 | 96.53 |
|                      | –                             | 95.24 | 96.87 |

The conversion at the onset of autoacceleration ( $X_m$ , Tables 1–3) increases with increase of the polymerization temperature, in accordance with published data [5, 24–27] and with the theory of polymerization of organized monomer systems [52, 53]. The theory [52, 53] states that the organization of monomers decreases with increase of the temperature, resulting in  $X_m$  shifting to higher value. From the results presented in Tables 1–3 it is evident that the polymerization temperature has a significant effect on the value of the conversion at the onset of autoacceleration.  $X_m$  increases with increase in the alkyl group length in the methacrylic acid ester (Table 4). The autoacceleration of MMA polymerization starts at conversion of about 24, in the case of EMA polymerization at 36, and in BMA polymerization at conversion of about 39 mass% (Table 4). Our results are in accordance with the published data [29–33].

The conversions at point K ( $X_k$ , Tables 1–3) increase with increase of the polymerization temperature, in accord with published data [26, 39–41]. Values of the final conversions for MMA vary from 90 to 99 mass% in the temperature range 60–90°C, for EMA from 94 to 99 mass% in temperature range 70–90°C, and for BMA from 93 to 97 mass% in temperature range 75–90°C. It was found [15, 54] that a correlation exists between  $X_k$  and the polymerization temperature and that 100% conversion could be achieved in bulk polymerization carried out above the glass transition temperature ( $T_g$ ) of the polymer. In the case of MMA polymerization at a temperature above  $T_g$ , the depolymerization becomes increasingly important [36]. Thus, a well-defined maximum at about 120°C can be observed in the plot of  $X_k$  vs. the reaction temperature [36]. The alkyl group length does not have a significant effect on the position of point K (Table 4). Some authors [5, 16, 29] have found that  $X_k$  increases

with increase in the alkyl group length in the ester. Our results do not confirm those findings.

**Table 4** Effect of alkyl group length on conversions at characteristic points of MMA, EMA and BMA polymerization ( $T=80^{\circ}\text{C}$ , 1 mass% AIBN)

| Conversion/<br>mass% | Alkyl methacrylates |       |       |
|----------------------|---------------------|-------|-------|
|                      | MMA                 | EMA   | BMA   |
| $X_m$                | 21.81               | 36.70 | 39.42 |
|                      | 24.48               | 36.66 | 38.10 |
|                      | 24.93               | 35.11 | 39.17 |
| $X_p$                | 62.90               | 67.79 | 65.11 |
|                      | 64.24               | 66.63 | 65.17 |
|                      | 63.61               | 66.93 | 66.74 |
| $X_s$                | 76.29               | 74.32 | 74.08 |
|                      | 76.90               | 74.95 | 74.05 |
|                      | 76.56               | 75.37 | 73.87 |
| $X_r$                | 92.55               | 93.92 | 91.85 |
|                      | 93.59               | 92.61 | 92.05 |
|                      | 93.46               | 92.93 | 91.14 |
| $X_k$                | 95.44               | 98.05 | 95.85 |
|                      | 95.48               | 97.32 | 94.60 |
|                      | 95.79               | 97.01 | 95.24 |

In all investigations published to date, all authors (except Schulz [18]) have paid attention to only two characteristic points: M and K. We consider, however, that points P, S and R (besides M and K) are of great importance for an explanation of the mechanism of free radical bulk polymerization of lower *n*-alkyl methacrylates. Schulz [18] determined the conversion at point S ( $X_s$ , the maximum in the polymerization rate) and concluded that  $X_s$  is independent of the initiator concentration, but increases with the polymerization temperature. Our experimental data (Tables 1–3) confirm that finding. The values of  $X_s$  are in the range of 70 to 80 mass% according to our presumptions [23] based on the theory of the polymerization of organized monomers. We earlier observed points P and R (the maximum and minimum in the autoacceleration) in the derived polymerization rate vs. time curve. The conversions at these points ( $X_p$  and  $X_r$ ) slightly increase with increase of the polymerization temperature, and the values of  $X_p$  and  $X_r$  are in accordance with our predictions [23] based on the polymerization of organized monomer systems. The alkyl group length does not have a significant effect on  $X_p$ ,  $X_s$  and  $X_r$  (Table 4).

In a recent paper [55] the conversions during the free radical copolymerization of methyl and lauryl methacrylates at the characteristic points of the reaction (points M, P, S and K) were determined. It was found that the conversions corresponding to the characteristic points are controlled by the length and composition of the polymer chains formed up to those points [55].

The experimental data concerning the effects of the polymerization temperature ( $T$ ) and the alkyl group length ( $C$ ) on the conversions at the characteristic points M, P, S, R

and K of MMA, EMA and BMA polymerization were statistically elaborated by regression analysis on a computer. The mathematical model 'Statmode 3' (JPC SOFTWARE) was used. The results of the regression analysis are given in Eqs (1)–(5):

$$X_m (\text{mass}\%) = -42.268 + 0.782T + 5.469C \quad (1)$$

( $SD=3.54\%$ ;  $R=0.96$ ;  $R_T=0.77$ ;  $R_C=0.76$ )

$$X_p (\text{mass}\%) = 34.582 + 0.348T + 1.205C \quad (2)$$

( $SD=1.76\%$ ;  $R=0.92$ ;  $R_T=0.85$ ;  $R_C=0.55$ )

$$X_s (\text{mass}\%) = 61.32 + 0.205T - 0.807C \quad (3)$$

( $SD=1.1\%$ ;  $R=0.87$ ;  $R_T=0.77$ ;  $R_C=-0.15$ )

$$X_r (\text{mass}\%) = 70.108 + 0.298T - 0.787C \quad (4)$$

( $SD=1.01\%$ ;  $R=0.94$ ;  $R_T=0.87$ ;  $R_C=0.04$ )

$$X_k (\text{mass}\%) = 75.789 + 0.263T - 0.445C \quad (5)$$

( $SD=1.08\%$ ;  $R=0.91$ ;  $R_T=0.89$ ;  $R_C=0.04$ )

where  $T$  is the polymerization temperature in °C,  $C$  is the number of carbon atoms in the alkyl group,  $R$  is the multivariable correlation coefficient,  $SD$  is the standard error,  $R_T$  is the partial correlation coefficient relating to the polymerization temperature and  $R_C$  is the partial correlation coefficient relating to the alkyl group length. It is desirable for  $R$  to be close to 1, but the values from 0.8 to 1 indicate that the correlation is very good. It is evident that the polymerization temperature has more significant effects on  $X_p$ ,  $X_s$ ,  $X_r$  and  $X_k$  than does the alkyl group length (the values of  $R_T$  are high in Eqs (2)–(5)). The conversion at the onset of autoacceleration ( $X_m$ ) depends similarly on the polymerization temperature and the alkyl group length ( $R_T=0.77$ ;  $R_C=0.76$ ; Eq. (1)).

## Conclusions

The effects of the polymerization temperature ( $T$ ) and the alkyl group length ( $C$ ) in the esters on the positions of the characteristic points M, P, S, R and K during MMA, EMA and BMA bulk polymerization were investigated.

It was found that the conversion at point M ( $X_m$ ) depends similarly on  $T$  and  $C$ .  $X_p$ ,  $X_s$ ,  $X_r$  and  $X_k$  depend much more on  $T$  than on  $C$ .

The experimental results given in this paper can be used to test the existing theories of autoacceleration.

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