

# The Concept of Conversion Distribution in Reactive Processing

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## SYNOPSIS

A new concept of conversion distribution applied to the continuous chemical modification and polymerization of polymers in a twin screw extruder was discussed. The kinetics and the residence time distribution function (RTD) are two undissociable parameters in reactive extrusion because their combination reflects the degree of homogeneity of the modified polymer at the die exit of the extruder. A function  $G$  defining the distribution of the modification rate allowed us to evaluate the distribution of the extent of the conversion around the mean conversion. This study has underlined the predominant role of the kinetics on the structural homogeneity of the modified product. This new concept was developed, within a framework of reactive processing, from previous works on chemical modification of polymers and polycondensation in corotating twin screw extruder. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Twin-screw extruders have been used as continuous reactors for polymer modification as well as for polymerization. Therefore, reactive extrusion was used as a new tool for the diversification of polymeric materials.<sup>1</sup> As reviewed by Brown and Orlando,<sup>2</sup> the types of reactions that have been performed by reactive extrusion may be conveniently divided into six categories: bulk polymerization, graft reaction, interchain copolymer formation, coupling or branching reaction, controlled molar mass distribution, and functionalization. In fact, all types of reaction in polymer synthesis can be carried out in an extruder provided that the kinetics of the chemical reaction can be adapted to the residence times of reactants in the extruder. However, continuous polymerization or polycondensation and chemical modification of the hydrocarbon skeleton are the two types of reactions which have been extensively developed on twin-screw extruders. Furthermore, residence times in any reactive continuous process

are characterized by a residence time distribution (RTD). The RTD describes the history of the polymer inside the extruder; the time the material spends in the extruder will be reflected in the quality of the product, the degree of mixing, the efficiency of the chemical reaction, and the extent of degradation. Therefore, the kinetics and RTD are two undissociable parameters in reactive extrusion because their combination may shed light on the degree of homogeneity of the modified polymer or polymerized polymer at the die exit of the extruder. Although recent advances were in progress concerning the modeling of a chemical reaction in a twin-screw extruder,<sup>3-6</sup> the degree of homogeneity of the final product was rarely approached except in the work of Stuber and Tirrel<sup>7</sup> on methyl methacrylate polymerization in a counterrotating twin-screw extruder.

From this point of view, a function  $G$  defining the distribution of the modification rate was introduced in a previous work on the chemical modification of poly(vinyl chloride) (PVC) in a twin-screw extruder.<sup>8</sup> More precisely, the breadth of distribution reflected the homogeneity of the modified polymer. The aim of the present article was to develop, within a framework of reactive processing, this new concept

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from any previous one on chemical modification of the polymer<sup>3,8</sup> and polycondensation in corotating twin-screw extruder.<sup>9</sup>

## CONCEPT

### Residence Time Distribution

The residence time distribution (RTD) can be described quantitatively with one function  $E(t)$ , which gives the response of an extruder to a pulse input at the inlet:

$$E(t) = \frac{C(t)}{\sum_0^{\infty} C(t)\Delta t} \quad (1)$$

where  $C(t)$  is the tracer concentration in the sample collected at time  $t$ , and  $t + \Delta t$  is the time interval between successive samplings. This function represents the age of the distribution of the polymer leaving the extruder.

On the other hand, the first moment from the origin, which is the measure of the average residence time  $\bar{t}$ , and the second moment about the average  $\sigma_t^2$  are usually considered.<sup>10</sup> From an experimental point of view, the problem of measuring the RTD function in a plastificator extruder has been extensively treated in the literature. Lastly, an ultraviolet method was developed<sup>11</sup> and successfully applied to PVC functionalization in a twin-screw extruder.<sup>8,12</sup> The originality of the method compared with classical ones was based on the grafting of the UV tracers (anthracene or phenyl group) onto the polymer backbone. Therefore, one can admit that the real RTD function of the polymer during the extrusion process was measured from this method. The main conclusion was that the RTD function of the graft tracer compared with the RTD of the free tracer shows a shorter mean residence time and a narrower distribution. Consequently, it is essential to control the determination of the RTD in reactive processing and mainly the tail of the distribution.

### Kinetics

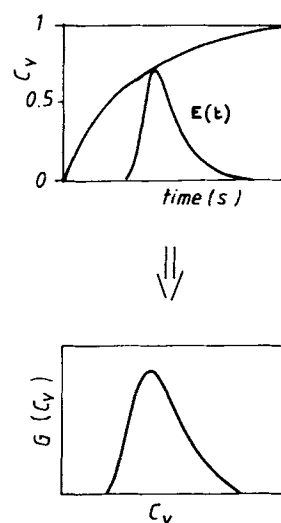
The second important parameter in reactive processing is the kinetics of the chemical reaction. The kinetics of the chemical modification of a melt polymer is generally obtained in a discontinuous system such as a batch reactor.<sup>3,13,14</sup> Then, a sample of reacting material is removed from the reactor, quenched, and subsequently analyzed, as, e.g., from

an IRFT technique. As discussed by Kim and White,<sup>3</sup> the kinetics obtained from this method may not be accurate due to the temperature gradient in the mixing chambers caused by the conception of the chamber itself and viscous dissipation of the melt polymer. Furthermore, the thermodynamical miscibility between reactants and polymers can be the source of heterogeneous reactive systems.

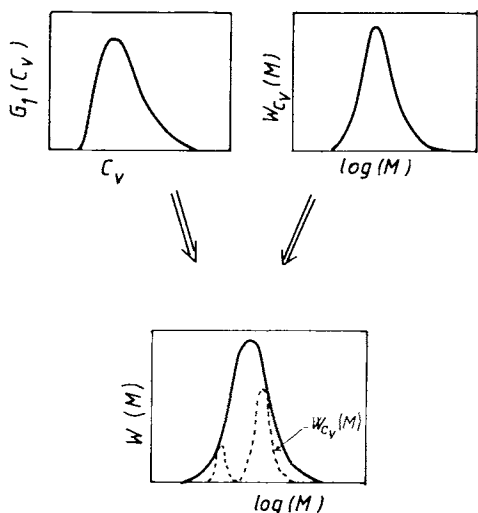
On the other hand, several methods have been used to monitor the kinetics of polymerization reactions. Extensive reviews have been reported by Kamal<sup>15</sup> and Mussati and Macosko.<sup>16</sup> The kinetics of a polymerization process is generally observed *in situ* in a heating cell of an FTIR apparatus. Good accuracy on the kinetics can be expected by this method.

### Conversion Distribution Function

From the RTD function and the kinetics of the chemical reaction, a function  $G(C_v)$  which describes the distribution of the conversion rate at the die exit of the extruder can be defined.<sup>8</sup> The RTD function gives the fraction of materials leaving the extruder with a residence time between  $t$  and  $t + \Delta t$ . Substituting the temporal parameter of the kinetic one by the extent of the reaction at time  $t$ , we defined the conversion distribution function  $G(C_v)$ . Such a function is illustrated in Figure 1. Then, the function  $G(C_v)$  gives the fraction of a modified polymer which has a chemical modification between  $C_v$  and  $C_v + \Delta C_v$ :



**Figure 1** The concept of the conversion distribution in reactive modification in the extruder.



**Figure 2** The concept of the conversion distribution in reactive polymerization in the extruder:  $W_{Cv(M)}$  is the molecular weight distribution of a polymer at the  $Cv$  homogeneous conversion.  $W_{(M)}$  is the molecular weight distribution of the polymer with a mean conversion of  $Cv$ .

$$G(Cv) = \frac{C(Cv)}{\sum C(Cv)\Delta Cv} \quad (2)$$

Two moments of the conversion distribution can be considered for its quantitative determination. The first moment from the origin expresses the measure of the mean conversion rate:

$$\bar{Cv} = \frac{\sum_{Cv_{min}}^{Cv_{max}} CvG(Cv)\Delta Cv}{\sum_{Cv_{min}}^{Cv_{max}} G(Cv)\Delta Cv} \quad (3)$$

Actually, the mean conversion rate is the conversion measured at the die exit including the effect of the distribution of conversions.

The second moment about the mean is the measure of the breadth of the distribution:

$$\sigma C_v^2 = \frac{\sum_{Cv_{min}}^{Cv_{max}} (Cv - \bar{Cv})^2 G(Cv)\Delta Cv}{\sum_{Cv_{min}}^{Cv_{max}} G(Cv)\Delta Cv} \quad (4)$$

This parameter expresses the homogeneity of the chemical conversion. Nevertheless, in the case of the polymer chemical modification, the breadth of the distribution is not quantifiable by any commercial instrument (or equipment) such as SEC. However, as shown in Figure 2, the shape of the distribution could be attempted in the case of a polycondensation process from the polymolecularity index by taking into account, e.g., the statistical methods

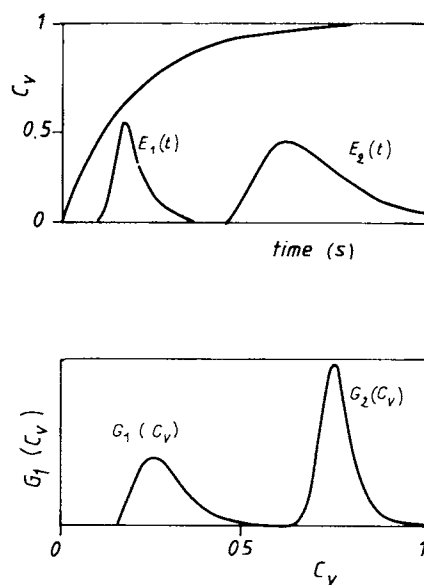
derived by Flory<sup>17</sup> to relate the molar mass distribution to a constant conversion  $Cv$ .

## RESULTS AND DISCUSSION

### Chemical Modification

The concept of the conversion distribution was first developed for the chemical modification of PVC by the grafting of a plasticizing group. As the kinetics law was monitored assuming that the variation of conversion at the exit of the extruder versus the average residence time in the extruder at different experimental conditions (reactant/PVC, screw speed) is representative of the kinetics, only a qualitative discussion was attempted from this work. However, the main conclusions remain valid: As shown in Figure 3, the shape of the kinetics law plays an important role in the homogeneity of the final modified product. Paradoxically, the calculated curves of the conversion distribution showed that the most homogeneous modified polymer was obtained with a low screw rotational speed although a low screw rotational speed presented a broader RTD. Considering the limit where the plateau conversion of the kinetic law is reached at the die exit of the extruder for all the reactants, a perfect homogeneous modified polymer can be obtained whatever the shape of the RTDs.

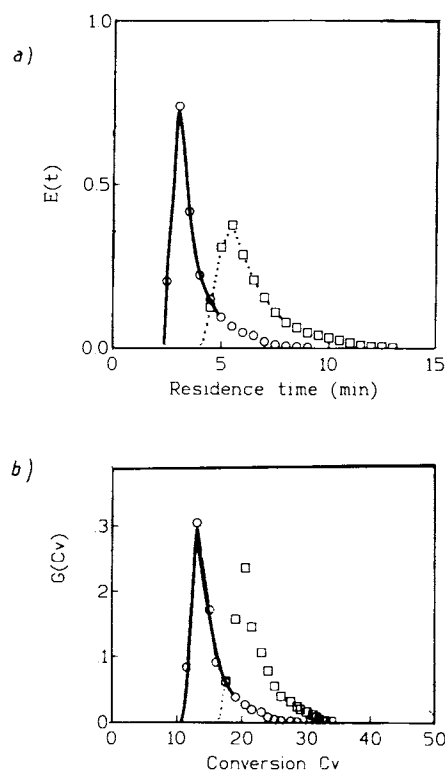
In the present work, this concept was developed for the works on transesterification of a ethylene



**Figure 3** Conversion distribution obtained from two different RTDs. Predominant effect of the kinetics on the conversion distribution.

vinyl acetate (EVA) copolymer with an aliphatic *n*-alcohol in a modular corotating twin-screw extruder recently reported by Kim and White.<sup>3</sup> From RTDs reported in their previous article<sup>18</sup> and the kinetics law obtained in a batch reactor, the values of the mean conversion rate and values of the breadth of the distribution are reported in Table I for the different configurations of the screws (screw speed: 30 rpm; feed rate: 1.41 kg/h).

The values of the mean conversion  $\overline{C}_v$  calculated from this concept are close to the values calculated by Kim and White from the fluid mechanism model of a modular corotating twin-screw extruder coupled with hypothetical reactor models representing the twin-screw reactive extrusion. The predictions of conversion are notably low compared to the experimental conversion data. The origins of the difference between experimental and predicted data were discussed by Kim and White.<sup>3</sup> However, the concept of the conversion distribution clearly shows that the chemical conversion of a polymer at the exit of the extruder is a mean conversion of a nonhomogeneous modified polymer. The predictions of the breadth of the conversion distributions are very sensitive to the tail of the RTD function. In Table I are compared predictions of  $\overline{C}_v$  and  $\sigma_{C_v}^2$  from experimental RTD and RTD including the tail of the distribution which has been estimated by the method developed by Todd.<sup>19</sup> As expected, the tail of the distribution has a slight influence on the predictions of the mean conversion and a high influence on  $\sigma_{C_v}^2$ . This result means that the determination and the prediction of the RTD are essential in order to elaborate predicting models on reactive processing. Consequently, a better control of the RTD through the elementary (right-handed, left-handed, and kneading) elements



**Figure 4** (a) RTD and (b) conversion distribution of the chemical modification of the EVA copolymer with an aliphatic *n*-alcohol with two different screw configurations noted 2 and 5 (see Table 1, Kim and White,<sup>3,18</sup>).

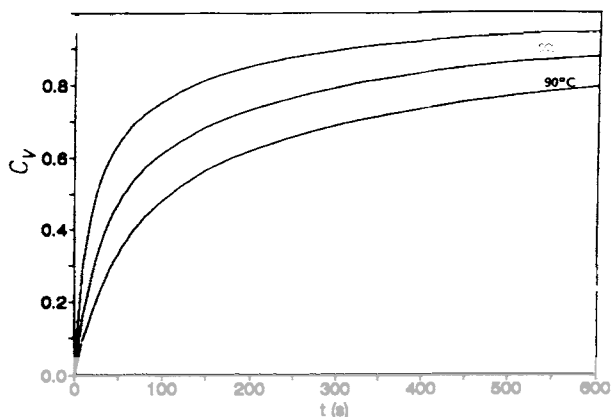
constituting the screws is required to limit further widening of the homogeneity of the final product.

On the other hand, in Figure 4(a) and (b) are compared the shape of the RTD with the shape of the conversion distribution for two-screw configurations noted 2 and 5 in Table I, respectively. Al-

**Table I** Chemical Modification of EVA by Transesterification: Experimental and Calculated Values,<sup>3,18</sup> Mean Conversion  $\overline{C}_v$ , Homogeneity of the Conversion  $\sigma_{C_v}^2$  from Experimental RTD and Including the Tail of the RTD at Different Screw Configurations

| Screw Configuration | Kim and White <sup>3</sup> |       | Present Study         |                  |                               |                  |
|---------------------|----------------------------|-------|-----------------------|------------------|-------------------------------|------------------|
|                     | Experimental Conversion    | Model | from Experimental RTD |                  | Including the Tail of the RTD |                  |
|                     |                            |       | $\overline{C}_v$      | $\sigma_{C_v}^2$ | $\overline{C}_v$              | $\sigma_{C_v}^2$ |
| 1 RHS only          | 19                         | 15.9  | 13                    | 4.2              | 13.1                          | 5.7              |
| 2 RHS + 2LHS        | 21.7                       | 16.3  | 15                    | 5.1              | 15                            | 9.1              |
| 3 RHS + HB          | 26.7                       | 18.3  | 17.5                  | 4.9              | 17.5                          | 9.9              |
| 4 RHS + 2KB         | 30.6                       | 20.8  | 21                    | 4.5              | 21                            | 11.05            |
| 5 RHS + 2KB + 1LHS  | 31.8                       | 21.3  | 22                    | 4.2              | 22.2                          | 11.03            |

RHS: right-hand side; LHS: left-hand side; KB: kneading block. See Kim and White.<sup>3</sup>



**Figure 5** Kinetic curves of the PACM system at  $T = 90$ , 105, and 125°C.

though the breadth of the two RTDs is very different, the conversion distributions exhibit only a slight difference in shape. This result means that the homogeneity of the polymer, chemically modified from the two configurations of the screws, is equivalent, which proves that the RTD must be combined with the kinetics of the chemical reaction to predict and control the homogeneity of the final product.

However, predictions of  $\sigma C_v^2$ , including the tail of the distribution, show that the screw configuration constituted only of right-handed screw elements gives the most homogeneous modification of EVA. This result is essentially true because the residence times of these different screw configurations are in the range of reaction times where the kinetics law varies approximately monotonous as  $dC_v/dt \approx Cte$ .

#### Polymerization and Polycondensation

Contrary to the kinetics of the chemical modifications previously described, the kinetics of polymerization in a twin-screw extruder must be sufficiently fast so that the monomer can go to nearly complete conversion in the limit of the residence time. As observed and predicted by Stuber and Tirrel,<sup>7</sup> the quality of the final product is directly dependent on the RTD: The polymer polymolecularity is increased for broader residence times. Generally, this effect on molar mass distribution (MMD) is true, but there are many other factors in reactive extrusion affecting MMD which are not completely understood. For instance, in the reactive extrusion of styrene polymers<sup>20</sup> and polyamide polymers,<sup>21</sup> no relationship between RTD and MMD was observed. On the other hand, the broader molar mass distribution of the polymer produced in the extruder can be attributed to the fact that mechanical degradation<sup>20</sup> and

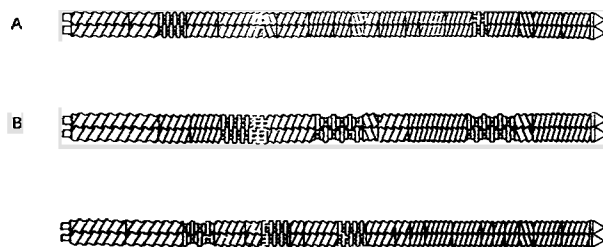
side reactions cannot be avoided at melt temperatures typically higher than 200°C.

The reactive system studied in the present work is a polycondensation based on a competitive reaction of a diamine (4,4'-diamine dicyclohexylmethane: PACM) with a diepoxy (bisphenol A diglycidyl ether: DGEBA) acting as a chain extender and a monoepoxy (glycidyl methacrylate: GMA) acting as a chain-termination agent, avoiding the gelation of the system and introducing double bonds in the prepared oligomer. We call it a PACM-based system. This system was studied in previous articles.<sup>9</sup> The system remains in a Newtonian rheological behavior along the extruder, although the viscosity changes typically from 1 Pa·s at the inlet to 10 Pa·s at the exit of the extruder. Thus, contrary to the chemical modification process of melt polymers, one can expect reduced interactions of kinetics and fluid dynamics and neglect the self-heating by viscous dissipation.

Furthermore, Figure 5 shows that the kinetics of the prepolymerization system PACM are suitable in order to elaborate these prepolymers in a twin-screw extruder at the temperatures of 90, 105, and 125°C.<sup>9,22</sup> The three-screw configurations used in this work are shown in Figure 6.

Screw profile A contains two short kneading-disc blocs and three independent left-handed screw elements. In profile B, three long kneading disc blocs were used. The second and the third of them are followed by left-handed screw elements. Profile C is designed with three short kneading-discs blocs and one independent left-handed screw element. In a previous work,<sup>9</sup> we showed a linear increase of average residence time with kneading discs blocs plus left-handed screw element length. We also noticed a mean residence time increase with the reaction temperature.

Using the RTD data and the kinetic modeling of the epoxy-amine reaction,<sup>9</sup> we calculated  $G(C_v)$ ;  $\bar{C}_v$  and  $\sigma C_v^2$  were calculated using eqs. (2)–(4). The results are reported in Table II. We first note a good

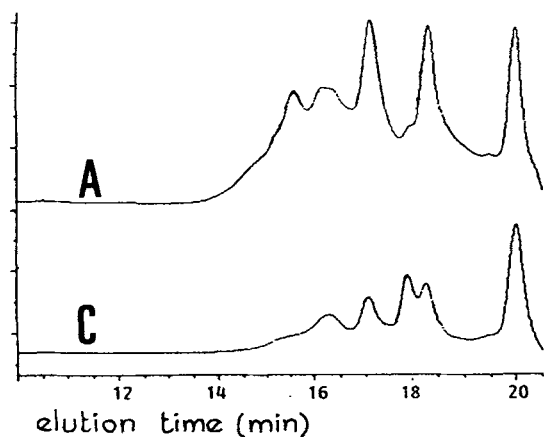


**Figure 6** Screw profiles used for the epoxy-amine multimethacrylic prepolymer synthesis.

**Table II** Reactive Extrusion PACM System: Mean Residence Time  $\bar{t}$ , Experimental  $Cv_{\text{exp}}$  and Calculated Mean Conversion  $\bar{Cv}$ , and  $\sigma_{Cv}^2$  at Different Temperatures for Three Different Screw Configurations,  $N = 33$  rpm and  $Q = 3$  kg/h

| Exp. | Screw Configuration | $T$ ( $^{\circ}\text{C}$ ) | $\bar{t}$ (s) | $Cv_{\text{exp}}$ | $\bar{Cv}$ | $\sigma_{Cv}^2$ |
|------|---------------------|----------------------------|---------------|-------------------|------------|-----------------|
| 1    | A                   | 105                        | 124           | 0.60              | 0.65       | 0.0021          |
| 2    | A                   | 125                        | 140           | 0.84              | 0.81       | 0.0010          |
| 3    | B                   | 90                         | 166           | 0.55              | 0.572      | 0.0060          |
| 4    | B                   | 105                        | 206           | 0.73              | 0.73       | 0.0024          |
| 5    | B                   | 125                        | 369           | 0.92              | 0.90       | 0.0012          |
| 6    | C                   | 90                         | 147           | 0.45              | 0.517      | 0.0380          |
| 7    | C                   | 105                        | 148           | 0.65              | 0.672      | 0.0380          |
| 8    | C                   | 125                        | 398           | 0.95              | 0.95       | 0.0015          |

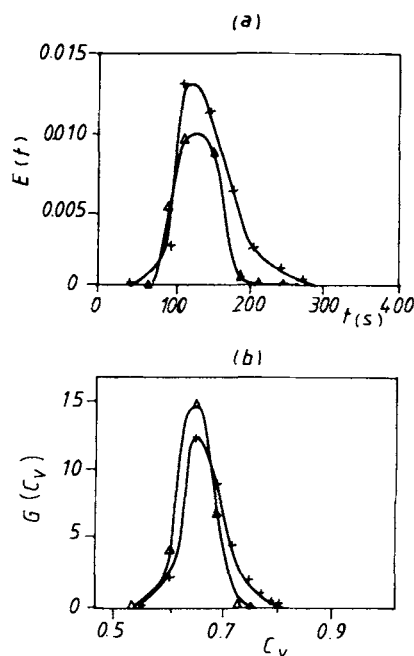
concordance between the measured  $Cv_{\text{exp}}$  and calculated  $\bar{Cv}$  for all experiments. This shows clearly that these reactions are kinetically controlled. Going into detail, for instance with experiments 1 and 7, we see that for these two reactions made at the same temperature ( $105^{\circ}\text{C}$ ) a similar  $Cv_{\text{exp}}$  and  $\bar{Cv}$  are obtained even if the  $\bar{t}$  are different. On the other hand, the  $\sigma_{Cv}^2$  values are quite different. Actually, the obtained products are very different as shown by their SEC chromatograms (Fig. 7). This is a consequence of different  $E(t)$  and  $G(Cv)$  (Fig. 8), meaning that the final product is the sum of variable amounts of different products. From this example, we see that, even if the RTD data are very useful, information concerning the conversion distribution are more representative of the chemical reactions occurring during the process.



**Figure 7** SEC of epoxy-amine multimethacrylic prepolymers prepared at  $105^{\circ}\text{C}$  using screw profiles A and C.

## CONCLUSIONS

A new concept of conversion distribution applied to the chemical modification of PVC and EVA and synthesis of methacrylic prepolymers in a twin-screw extruder was discussed. Then, the combination of the RTD function with the kinetics of this chemical reaction allowed us to evaluate the distribution of the extent of the conversion around the mean con-



**Figure 8** (a) RTD and (b) conversion distribution of epoxy-amine multimethacrylic prepolymers prepared at  $105^{\circ}\text{C}$  using screw profiles ( $\Delta$ ) A and ( $+$ ) C.

version. This conversion distribution and, more precisely, the breadth of this distribution, reflects the homogeneity of the final product at the exit of the extruder. This work has underlined the predominant role of kinetics on the structural homogeneity of the product. Actually, the duality residence times and chemical kinetics must be taken into account for the analysis of the homogeneity of the product at the end of this reactive elaboration. Nevertheless, the approach of the conversion distribution from the global RTD should be improved by integrating in the development of this concept the local RTDs of the different screw elements constituting the screws.

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