Some Aspects on Polymerization in a Bubble Gas Column Reactor

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Abstract

A particularly important role in the chemical industry is played by the column-type reactors, which are successfully used in most of the industrial, especially transfer, processes. But the utilization of the column-type reactors for the polymerization reactions started its development only recently. The polymerization process, which take place in a column type reactor is very complex due to the intergrowth of two types of factors: those which usually influence radical polymerization and those which are specific for the chosen polymerization process The inner stirring may be achieved by different mechanical means or by bubbling a gas. This study tries to establish a correlation between some factors that influence the polymerization in a bubble gas column reactor of some acrylic monomers: the size of the gas bubbles, packing material, jacket temperature. The resulting polymer, used in paints and lacquers industry, is free from residual monomer.

Key words: bubble, column-type reactor, packing material, temperature

1. Introduction

A particularly important role in the chemical industry is played by the column-type reactors, which are successfully used in most of the industrial, especially transfer, processes. But the utilization of the column-type reactors for the polymerization reactions started its development only recently. The inner stirring may be achieved by different mechanical means or by bubbling a gas.

The bubble column reactors were used in different processes by many authors. Rune-ngam D.[1], Majumder S.K. [2], Jin H. [3], Worski S. [4], Laakkonen M. [5] analised the bubble behavior in bubble columns, the influence of the medium on bubble size, the influence of the bubble size on the process hydrodynamics. Kazakis N.A. [6] analysed the influence of the medium viscozity on the bubble flow regime, Mitropetros K. [7] performed a study on the bubble cinetics in a bubble column reactor, Lin T.J. [8] made a also a quantitative study on hydrodynamics of the bubbles.

Kamadieva R. [9] studied the performance of a bubble column with and without packing material.

The copolymerization processes may be intensified by stirring using mechanical stirrers and it has been found that by intensifying the stirring it was increased the diffusion degree of the monomers. Also, the presence of an inert gas in the reaction medium favors the polymerization process.

The free volume of the packing is an important parameter for emphasizing the increase of the efficiency of the solution polymerization processes in presence of packing. Under the polymerization conditions a packing is efficient if it is characterized by as high as possible specific surface and free volume, which means optimum conditions for the diffusion phenomena. Temperature is an important factor in the polymerization reactions. The reaction rate and the polymerization degree depend on the temperature at which the reaction is carried out.

In this paper is presented the utilization of a column-type reactor for the solution copolymerization, where the stirring is achieved by bubbling an inert gas [10, 11]. The influence of the diameter of the gas bubbling nozzle on the process efficiency and the influence of various packing types on the process are analyzed.

The present paper also presents the influence of temperature on the solution polymerization of methyl methacrylate and butyl acrylate in a column reactor with stirring by inert gas bubbling.

The hydrodynamic behavior of a gas bubble is variable and complex, due to the continuous change of shape, as a result of the forces acting on it. The flow pattern of the bubble is characterized by the Reynolds criteria (eq.1):

$$\mathrm{Re} = \frac{w_0 d_b \rho_m}{\eta_m} \qquad (1)$$

where: w_0 - the climbing speed of the bubble, m/s
ρ_m – density of the medium, kg/m^3
η_m - viscosity of the medium, Pa.s
d_b – diameter of the gas bubble (eq.2), m

$$d_b = \sqrt[3]{\frac{6 d_0 \sigma_m}{\rho_m g}} \qquad (2)$$

where: d_0 – diameter of the nozzle orifice, m
g – gravity acceleration, m/s^2
σ_m - surface tension of the medium, N/m

The results obtained for the copolymerization of butyl acrylate with methyl methacrylate in a column-type apparatus by studying the influence of stirring and the type of packing materials on the process are presented below. The stirring has been achieved by bubbling nitrogen (which is also the inert gas), introduced into the reaction medium through nozzles of different diameters.

2. Materials and Method

The experimental determinations have been carried out in a column-type apparatus provided with heating jacket.

As monomers have been used butyl acrylate (BA) and methyl methacrylate (MM) in 6 : 4 ratio ; toluene was the solvent, and benzoyl peroxide (BPO) the initiating agent of the copolymerization reaction. The reactants have been introduced in the column and the experiments have been carried out at a temperature of 96^{o}C.

It has been performed the copolymerization of BA and MM without bubbling of nitrogen, and after that experiments have been carried out introducing nitrogen at the bottom of the column through central nozzles of different diameters and by the utilization of different types of packing. The temperature was modified between 85 and 97°C.

3. Results

The results of the experimental research are as follows:

3.1. The İnfluence of Central Nozzles Diameter

Figure 1 presents the dependence of polymerization rate on nozzle diameter:

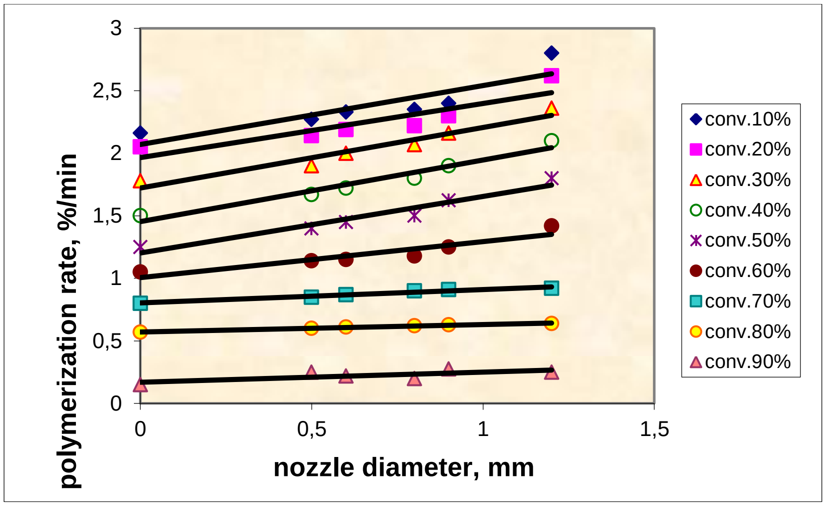

Figure 1. Dependence of polymerization rate on nozzle diameter

It was found that the slope of the straight lines is approximately constant, (with an average value of about 0.46), up to fairly high conversions (approximately 50%), hence the polymerization rate rises constantly with increasing the nozzle diameter, together with the progression of the reaction.

In **Table 1** are listed the equations of the straight lines which represent the variation of the polymerization rate with respect to the diameter of the nitrogen gas bubbling nozzle, at different conversions:

Table 1. Dependence equations between the polymerization rate and the diameter of the nozzle through which nitrogen is bubbled, at different conversion, at constant nitrogen pressure

Conversion, %	v_p = f (nozzle diameter)
10	y = 0.47 x + 2.07
20	y = 0.43 x + 1.96
30	y = 0.48 x + 1.72
40	y = 0.49 x + 1.45
50	y = 0.45x + 1.20
60	y = 0.29 x + 1.01
70	y = 0.11 x + 0.8
80	y = 0.06 x + 0.57
90	y = 0.08 x + 0.17

A systematic increase of the density and viscosity with the increase of conversion, will also affect the diameter of the bubble climbing up in the column, as well as the hydrodynamic pattern of the bubbles in the column. During the progression of the reaction the diameter of the bubbles becomes smaller, as well as their velocity. Since the number Re depends on density, viscosity and bubble diameter, the variation of the flow pattern of the gas bubbles during the increase of conversion is as presented in **Figure 2**, that is, a decrease with time, the initial value depending on the initial conditions of the different experiments, respectively on the diameter of the bubbling nozzle for the nitrogen gas.

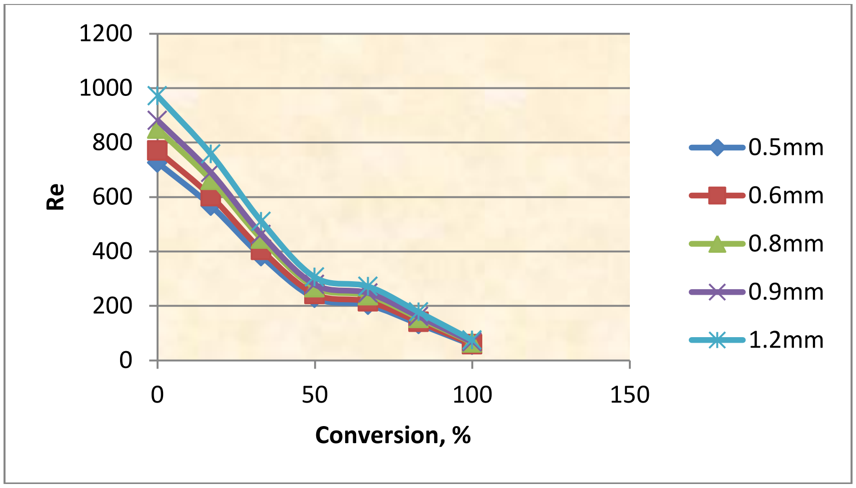

Fig.2. Dependence of Re criteria on conversion

3.2. The influence of Packing Material

There have been used different packing, the characteristics of which are listed in **Table 2**.

Table 2. The characteristics of the packing material

Type of packing	Sizes, mm	Free volume, m^3/m^3	Specific surface, m^2/m^3
Large beads	6.37	0.42	509
Small beads	4.0	0.40	850
Raschig rings	8 x 9.3 x 1	0.70	875
Wire spirals	4 x 4 x 0.5	0.77	970

It has been concluded that different packing used influence the polymerization, determining either the intensification of the process (Raschig rings, beads), or its inhibition (wire spirals). The polymerization rate in presence of wire spirals is lower due to the interference between the spiral material and the other components of the system.

The results concerning the influence of the other types of packing on the studied copolymerization process are presented below.

Figure 3 presents the dependence of conversion velocity on conversion:

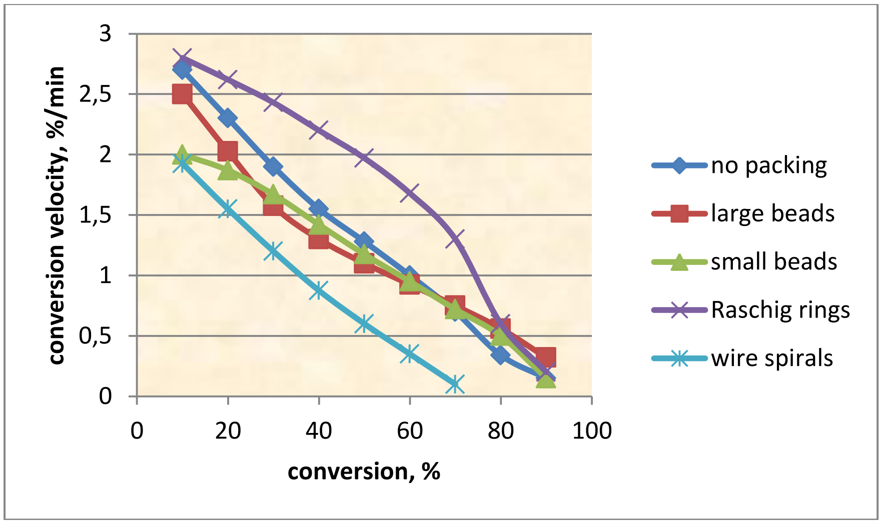

Figure 3. Dependence of conversion velocity on conversion

3.3. The İnfluence of Jacket Temperature

As it has been expected, for all the cases conversion increased very much at the beginning of the reaction, further on tending to a constant value. It is also to be noted that with the increase of the reaction temperature conversion reaches the maximum value in shorter time.

In **Table 3** is presented the variation of the reaction rate on time and on the conversion degree.

Table 3. Variation of the reaction rate on time and on the conversion degree

Time [min]	Conversion [%]	Reaction rate [%/min]					
		85°C	**91°C**	**94°C**	**95°C**	**96°C**	**97°C**
7	10	1.2	1.76	2.5	2.7	3.15	3.6
17	20	0.85	1.34	2.05	2.45	2.9	3.3
30	30	0.7	1.05	1.57	2.15	2.6	3.15
45	40	0.55	0.73	1.28	1.8	2.2	2.8
65	50	0.48	0.6	1.06	1.4	1.7	2.15
88	60	0.45	0.55	0.86	0.93	1.1	1.57
116	70	0.4	0.45	0.503	0.5	0.6	1
148	80	0.35	0.3	0.275	0.3	0.4	0.5
150	90	0.2	0.2	0.2	0.15	0.25	0.3

In **Table 4** are given the times required for reaching the conversion of 85 % as function of temperature

Table 4. Reaction times to reach the conversion of 85 % as function of the working temperature

Nr.	Temperature, °C	Time, min
1	85	170
2	91	135
3	94	97
4	95	87
5	96	73
6	97	60

One observes that as temperature rises, the time for reaching a high conversion decreases significantly and this implies the increase of the installation output with the increase of the working temperatures.

As the temperature increases and the reaction proceeds, the solution density and viscosity modify, as well as the Re number of it; the variation of which with respect to temperature and conversion is presented in **Table 5**.

Table 5. Dependence of the Re number of the gas bubble on conversion degree, at different temperatures

Conversion [%]	Re		
	85°C	**91°C**	**96°C**
0	729	750	771
16	562	575	602
33	363	386	404
50	211	225	242
66	190	205	215
83	121	132	140

100	48	53	60

From the analysis of the above graphic representations one notes that the density and viscosity increase with the progress of the polymerization reaction, but the values are lower as the temperature is increased and this determines the bubble diameter to increase with the temperature increase but decreases with the progress of the process. Quite alike, the ascension velocity of the bubbles, respectively the value of the number Re for the gas bubble will become lower with the higher conversion, but will have higher values at higher temperatures.

IR spectra, performed with a SPECORD apparatus, and the ^{1}H-NMR spectra, performed with a JEOL spectrometer at 60Hz, in $CDCl_3$ solution, filtered at room temperature, show that in the final copolymer the bands: 1380 – 1420; 1630 – 1680; 1800 – 1860; 2990 – 3100 cm^{-1}, and the pics: 2-3 mm, corresponding to the doublebonds in the unreacted monomers, are lower or even do not exist anymore (1630 - 1680; 1800 – 1860), when working with stirring with bubbling nitrogene, compared with the case without this kind of stirring. So, the resulting polymer, used in paints and lacquers industry, is free from residual monomer.

4. Discussions

During this research has been carried out the copolymerization of butyl acrylate with methyl methacrylate in solution, using toluene as solvent and benzoyl peroxide as initiating agent for the reaction.

Stirring has been achieved by bubbling nitrogen gas at the bottom of the column through nozzles of different diameters, thus providing also an inert medium.

Interpretations have been proposed concerning the kinetics of the process, finding that as the bubbling nozzle diameter increased, the conversion reached faster the maximum value, hence the process rate was higher. The rate increases constantly with the nozzle diameter, for the same conversion the variation being linear.There have been calculated the diameters of the bubbles, their velocities and the Re numbers for all the experimented cases. It has been found that these lower with the progression of the reaction, since both the density and viscosity of the medium become higher.

It has been established that stirring has a favorable effect on the polymerization, resulting in the intensification of the process.There have been used different types of packing in order to intensify the process and it was found that this exerted a significant influence of the development of polymerization.It has been shown that from the two main characteristics of the packing, respectively the free volume and the specific surface, the most significant influence on the polymerization reaction was exerted by the former, while the influence of the latter was less important.Thus, for the packing consisting of balls, either large or small, although the specific surfaces are very unlike and the free volumes are close, the values of the reaction rates are quite similar.By comparing the packing consisting of small balls with that consisting of Raschig rings, which are of close specific surfaces, but very different free volumes, it has been found that the polymerization rate was different, which means that the free volume exerted a pregnant influence on it.If the process has been carried out without packing (that is, at the maximum free volume) it has been found that, unless at the beginning of the process the reaction rate was higher than that when using a Raschig rings packing, in short time it became lower. This is due to the absence of packing, respectively of a contacting surface between the reactants which to favor the transfer process (the latter being intensified with increasing specific surface).Over a certain duration of the process the polymerization rate is less influenced by the presence of packing. This may be explained by the lowering of the monomer concentration and increased polymer amount in the mixture, which results in a competition between translational and segmental diffusion.

The working temperature has been varied between 85 and 98^{o}C. It has been found that temperature influenced significantly both the working time and the rate of copolymerization of butyl acrylate and methyl methacrylate, both of them increasing with the temperature rise.

When choosing the working temperature one must consider the output, the possibility to recover the heat of reaction and the properties required for the copolymers in use.

Conclusions

The paper presents the kinetics of the polymerization in a bubble column reactor, introducing nitrogen (as a stirring mean and an inert medium as well) through nozzles of different diameters. The hydrodynamics of the bubbles, the influence of different packing materials and the influence of the temperature on the process are also presented.

Accordind to the IR and the ^{1}H-NMR analyses, when working with stirring with bubbling nitrogene, compared with the case without this kind of stirring the resulting polymer, used in paints and lacquers industry, is free from residual monomer.

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