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Influence of NaCl on the polymerization of vinyl monomers by the suspension process

Influencia del NaCl en la polimerización de monómeros vinílicos por el proceso de suspensión

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Abstract

The production of artificial polymers is, today, one of themost important activities of the chemical industry, polymersare widely used in everyday life, as, there are different types of polymers, they can be used for different uses. These polymeric materials have unique mechanical, physical and chemical properties, which most other materials do not possess, not to mention that its cost is lower than the other materials. The present research work focuses on the determination of optimal operating conditions for the polymerization of styrene and methyl methacrylate in a Batch reactor, as well as the influence of inorganic salt in this case NaCl in the performance of reaction and in the size of the material polymer, through the process of suspension using a synthetic route of polymerization by radical free conventional (FRP), where viscometry to the polymeric material testing was performed for this way characterize it, and to determine factors of interest such as the molecular weight, etc.

Styrene, Methyl methacrylate, Polymerization, Suspension process, Free radicals

Resumen

La producción de polímeros artificiales es, en la actualidad, una de las actividades más importantes de la industria química, los polímeros son usados ampliamente en la vida cotidiana, ya que, al existir diferentes tipos de polímeros, pueden ser aprovechados para diferentes usos. Estos materiales poliméricos tienen singulares propiedades mecánicas, físicas y químicas, que la mayor parte de otros materiales no poseen, sin mencionar que su costo es menor al de otros materiales. El presente trabajo de investigación se enfoca en la determinación de condiciones de operación óptimas para la polimerización de estireno y metacrilato de metilo en un reactor Batch, así como también la influencia de una sal inorgánica en este caso NaCl en el rendimiento de reacción y en el tamaño del material polimérico, mediante el proceso de suspensión utilizando una ruta sintética de polimerización por radicales libres convencionales (FRP), donde se le realizaron pruebas de viscosimetria al material polimérico para de esta manera caracterizarlo , y poder determinar ciertos factores de interés como el peso molecular, etc.

Estireno, Metacrilato de metilo, Polimerización, Proceso de suspensión, Radicales libres

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Introduction

Polymers, synthetic or natural are present in every aspect of our lives, in many modern materials, pharmaceutical equipment, electronic devices, automotive parts, medical equipment, etc. From time to date, polymers have been replacing traditional materials, mainly at low cost and the possibility of being adapted in a host of special applications.

Therefore, at present, the polymers area in the world is one of those with the highest growth due to the demand of its products in the international market, which is why this sector needs to invest in research and technology to improve the processes of obtaining their products.

In the present research work the synthesis of the polymers was carried out by means of the process of free radical suspension (FRP), it is a very important commercial process for the preparation of polymers with high molecular weight because it can be used for the polymerization of a wide variety of vinyl monomers under moderate reaction conditions, requiring absence of oxygen, but is water tolerant, and can be carried out over a wide range of temperatures (-80 to 250˚C).

Radical polymerization, like other chain growth polymerization mechanisms, has three main reactions: initiation, propagation and termination.

The initiation of a free radical polymerization consists of two steps. In the first, the initiator (I) is broken down into two radical species. In the second step of the initiation, a monomer molecule (M) reacts with the radical initiator to form a radical monomer. Propagation is the growth of the active chains (radicals) by a sequential addition of monomers. And the termination produces dead polymer chains: the growth of the polymer chains is finished and the active centers are irreversibly annihilated.

As mentioned in this work we focus on the suspension polymerization, where the monomer to be polymerized has to be dispersed in the continuous phase (aqueous phase) as small droplets.

To achieve a stable dispersion with a controlled coalescence of the droplets during the polymerization process, this is achieved by applying a suitable method of agitation in the reactor and by means of the use of suspending agents (stabilizing or dispersing agents).

Both the production of polystyrene (PS) and polymethyl methacrylate (PMMA) are some of the most important polymeric materials available today, so the industrial production of PS and PMMA has led to a large amount of development and sustainable growth as a mature technology.

Overall objective

Obtain polymers of styrene and methyl methacrylate by the process of suspension via free radicals, varying the reaction parameters, such as temperature, speed of agitation, etc. To determine the performance of the reaction.

Specific objectives

- Synthesize polystyrene beads, determining the optimal operating conditions for subsequent characterization.
- Synthesize polymethyl methacrylate beads to determine optimal operating conditions for further characterization
- Determination of the reaction yield.

Materials and methods

REAGENTS

Monomers> Styrene and methyl methacrylate: With a purity percentage> 99% (Sigma-Aldrich).

Washing> Hydroxide sodium 0.1M (HYCEL)

Dispersing agent> Polyvinyl alcohol (PVA). Hydrolysis percentage: 87-90%. (Sigma-Aldrich).

Initiator> Benzoyl peroxide: With a purity percentage of 97%. (Sigma-Aldrich).

Solvent> Toluene.

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Polymerization of styrene

Determination of operating conditions: The polymerization process was followed by suspension via FRP. The reactions were carried out in a 500 mL Batch reactor, using for the continuous phase a constant volume of 240 mL of distilled water with a PVA concentration of 5 g / L, and adding different amounts of salt (NaCl), 0 g, 0.3 g, 0.45 g. While for the dispersed phase, 20 mL of styrene was added, with equal amounts of initiator (BPO); 0.325 gr (ratio 1: 130). The synthesis was carried out with a stirring speed of 150 rpm at a temperature of 85 ± 5 ° C for 2.45 hours and 3.00 hours consecutively.

Polymerization of methyl methacrylate

In the same manner, for this reaction, suspension polymerization was followed via FRP. The reactions were carried out in a 300 mL reactor, and using a constant volume of 110 mL of distilled water with a PVA concentration of 5 g / L for the continuous phase, and adding different amounts of salt (NaCl), 0 g and 0.3 g. While for the dispersed phase, 8 mL of methyl methacrylate was added, with an amount of initiator (BPO); 0.1818 gr (ratio 1: 100) and. The synthesis was carried out with stirring speeds of 420, 500 rpm at a temperature of 75 ± 5 ° C, for 1.00 hours and 1.30 hours consecutively.

Performance of the reaction

The yield of polystyrene and polymethyl methacrylate obtained with the following equation was calculated.

$$\%R = \frac{W_{MO}}{W_P} x100$$

Where:

% R is the percentage of performance

W_{MO} is the weight of the polymer obtained, gr in the reaction.

W_P is the weight of the monomers obtained theoretically in, gr.

Characterization

Viscosimetry The average molecular weights were determined with an Ostwald viscometer number 150 and the Mark-Houwink equation. The constants used for toluene styrene systems: $\alpha = 0.62$ $k = 0.037$ and for the methacrylate methyl-toluene system: $\alpha = 0.73$ $k = 0.0071$.

Results and Discussion

Experimentally, the reactions were performed with the styrene and methyl methacrylate monomers with different volumes of PVA and BPO, in a Batch reactor, at different stirring speeds of 150, 420 and 500 rpm and at 85 ± 5 °C.

The variations were made in each of the reactions until obtaining the optimum conditions of operation where pearls were obtained with good appearance and of considerable size and the reactions that were more favourable of the different polymers were selected and analysed.

The influence of temperature and polymerization time on the final molecular weight is not so significant when adding the inorganic compound (sodium chloride, NaCl) in the reaction medium, so it was not considered in the analysis of results. however, the influence that the agitation speed has if it is of consideration.

For example, the **Table 1** and **Figure 1** show the data obtained from the capillary viscosimetry to determine the molecular weight of the PS at 150 rpm and 0 g of NaCl added in the reaction medium.

Concentration (g/mL)	η_r (t/t_0)	η_{sp} ($t-t_0/t_0$)	η_{red} (η_{sp}/c)	η_{inh} In η_r/c
0.002	1.06	0.06	27.85	27.10
0.001	1.04	0.04	38.35	37.63
0.0005	1.03	0.03	50.66	50.04
0.00025	1.02	0.02	76.14	75.42

Table 1 100% Polystyrene

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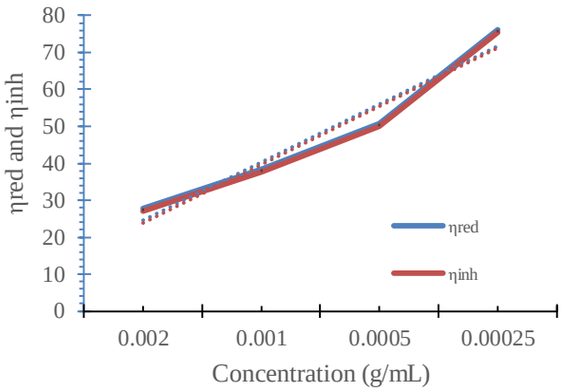


Graph 1 100% Polystyrene

The determination for molecular weight was made using the parameters offered by the Mark-Kouwink expression, that is (see **Table 2**):

[η]	α (Toluene at 298°K)	*k* PS (10^{-3})	M_v (([η]/K)^(1/α))	M_w (1.2M_V)
76.17	0.62	37	1013x10^3	1317x10^3

Table 2 100% Polystyrene

The yield of polystyrene obtained was 56.8% which is an average performance can be considered good, so we would have to check or refine some details technically. The M_w was 1317x10^3 g/mol which is a very high molecular weight.

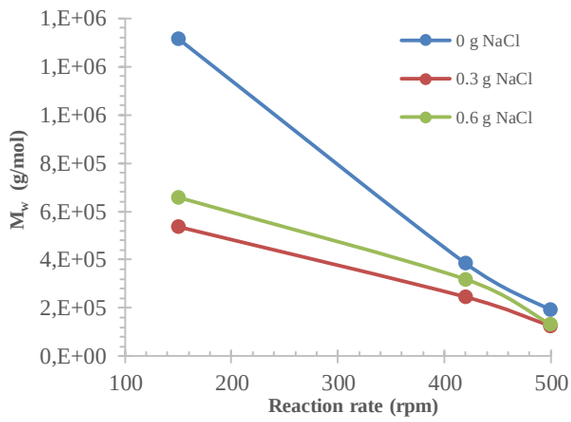
As a summary form, **Table 3** shows the molecular weights for the polystyrene obtained by the suspension process at different reaction rates and amounts of the inorganic salt.

Rx	NaCl (g)	*Reaction rate (rpm)*	M_w x 10^{-3} (g/mol)
1	0	150	1316
2	0	420	385
3	0	500	191
4	0.3	150	539.8
5	0.3	420	245.6
6	0.3	500	125
7	0.6	150	658.5
8	0.6	420	318.7
9	0.6	500	131.7

Table 4 Summary of the molecular weights for the PS by the process of suspension at 85 °C

The influence of the rate of agitation and the amount of sodium chloride in the reaction medium can be seen in **Figure 2**, clearly observing how the flocculating effect of the inorganic salt (cage effect) remains very intense as the amount of ions in the reaction medium; however, there is a limit of this amount and it is observed with 0.6 g of NaCl.

This is because the medium is already saturated, the effect is already minimal with the size of the polymer chain, which no longer allows it to continue to grow in the process of chain propagation.



Graph 2 Evolution of the Mw of the PS in the process of suspension at different concentrations of NaCl and agitation speed at 85 ° C

The tendency that can also be observed is that as the speed of agitation increases in the medium, the molecular weight decreases, which is correct because there is a greater breakage of the pearls formed in the process of suspension; that is, the size of the particles is smaller as the agitation speed increases, so there is less volume to store a greater amount of monomer. Likewise, coupled with the presence of NaCl, the space is diminished and therefore, there is a lower molecular weight of the polymer chains formed.

Similarly, **Table 5** presents the data acquired for PMMA at 85 ° C of molecular weight at different inorganic salt concentrations and agitation rates.

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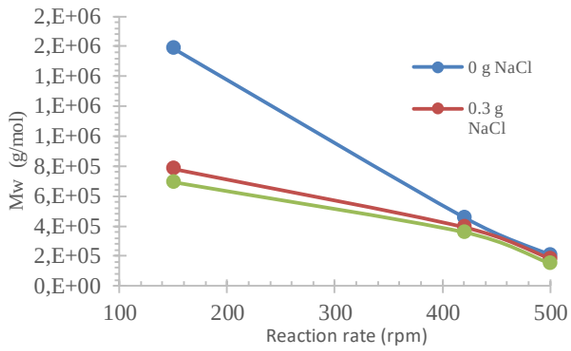
Rx	NaCl (g)	*Reaction rate (rpm)*	M_w x 10^{-3} (g/mol)
10	0	150	1586.1
11	0	420	457.7
12	0	500	206.6
13	0.3	150	781
14	0.3	420	392.1
15	0.3	500	183
16	0.6	150	693.1
17	0.6	420	359.8
18	0.6	500	149.7

Table 5 Summary of the molecular weights for the PMMA by the process of suspension at 85 ℃

The yield of methyl polymethacrylate obtained was 77% average which is a yield under the operating conditions were favorable for the reaction. Considering that the propagation constant that MMA has is much greater than that of styrene, which denotes that the reaction time is shorter to obtain this conversion; Likewise, a similar behavior is observed in the evolution of molecular weight with respect to the agitation value and the concentration of the inorganic salt (see **Figure 3**).



Graph 3 Evolution of the Mw of the PMMA in the process of suspension at different concentrations of NaCl and agitation speed at 85 ° C

However, the effect of sodium chloride as a flocculating effect in MMA is not very appreciable at high concentrations and this is due to the electrostatic forces presented by the inorganic salt with the ester group present in the monomer, indicating that the critical concentration in this case is 0.3 g NaCl.

Conclusions

By way of conclusion we can say that through this work it was observed that for the polymerization performance of styrene and methyl methacrylate it is important, the presence of the dispersing agent since it avoids the agglomeration or coalescence of the polymer beads.

Because when decreasing this agglomeration we will have mostly pearls and a better performance in the reaction, with respect to the inorganic salt that in our case the NaCl, we can say that it was mostly favorable in the styrene polymers, not so much for the methyl methacrylate, but in if it is a good influence on the size of polymeric material and influences its consistency.

Another important factor is the agitation speed that influences the formation of beads and molecular weight. Based on this, it was possible to obtain the most adequate operating conditions for the process, giving as a good result that the suspension process is a good way to obtain this type of polymers.

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