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EMULSION COPOLYMERIZATION OF VINYL ACETATE AND BUTYL ACRYLATE IN A TUBULAR REACTOR

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Cette thèse intitulée :

EMULSION COPOLYMERIZATION OF VINYL ACETATE AND BUTYL ACRYLATE IN A TUBULAR REACTOR

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en vue de l'obtention du Diplôme de: Philosophiae Doctor

a été dûment acceptée par le jury d'examen constitué de:

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DÉDICACE

To my parents for their full support during my life,

to my wife Ziba for her kindness, patience and encouragement,

and to my beloved little girl, the present of god, Yasaman

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RÉSUMÉ

La polymérisation en émulsion est un procédé commercialement important. Au cours de la seconde guerre mondiale des recherches intensives ont été effectuées pour développer et obtenir un latex synthétique capable de remplacer le caoutchouc naturel. De nos jours, le procédé de polymérisation en émulsion est à la base de produits dont le domaine d'applications n'a fait que sétendre. A cause de la grande souplesse du procédé, ayant (entre autres) de l'eau comme milieu de dispersion de meilleurs résultats peuvent être atteints. Parmi les produits obtenus par le procédé d'emulsion, ou peut citer le caoutchouc synthétique, la peinture latex, les adhésifs, la cire à plancher, des enduits imperméabilisants, des additifs pour le béton, ainsi que de nombreuses applications dans le domaine médical tel que des médicaments à effets contrôlés.

La polymérisation en émulsion a bien été étudiée dans les systèmes en cuvée et à un degré moindre dans les réacteurs à réservoir à agitation continue (CSTR); cependant, très peu de recherche ont eu lieu avec les réacteurs tubulaires. Ceci est un peu surprenant du fait du potentiel d'un tel système.

L'objectif principal du travail proposé est d'étudier le copolymérisation d'acétate de vinyle et l'acrylate de butyle dans un réacteur tubulaire. Les objectifs spécifiques sont les suivants:

- établir les meilleures conditions d'utilisation d'un un réacteur tubulaire avec et sans agitateur statique.

- évaluer l'effet de l'agitateur statique sur les caractéristiques du produit, et sur la distribution de la taille des particules.
- déterminer l'effet de paramètres d'opération sur la distribution de la taille de particule et la composition du copolymère .

Comme dans le cas du styrène et de l'acétate de vinyle, un écoulement et une conversion maximale est obtenue dans certaines conditions d'agitation pour la polymérisation de l'acétate de vinyle avec l'acrylate de butyle. Non seulement l'agitation mais aussi la composition du mélange de réactifs avait une incidence sur la région du maximum de la conversion. De plus la quantité d'acrylate de butyle a un effet direct sur le nombre de particules ainsi que sur la conversion finale. Pour de faibles niveaux en acrylate de butyle, la vitesse d'écoulement à l'intérieur du tube a un effet important sur la forme et la largeur de la distribution de la taille des particules. Cet effet peut varier selon la concentration de l'acrylate de butyle et de la vitesse d'écoulement. Les résultats obtenus pour la composition du copolymère ont montré que dans la plupart des expériences, un copolymère bloc alterné est formé pendant la réaction.

La copolymérisation en présence d'un agitateur statique a été évaluée en comparant les valeurs obtenues en présence et en absence d'un agitateur statique. On a trouvé qu'il y avait une zone d'écoulement dans laquelle une conversion maximale est obtenue. Cette région peut être déplacée en changeant la composition de l'alimentation, et en ajoutant un agitateur statique. L'agitateur statique change la distribution de la taille des particules dans le latex final, ainsi que la structure moléculaire du produit.

Les rapports de réactivité apparents de l'acétate de vinyle avec l'acrylate de butyle ont été déterminés pour des régions d'écoulement différentes en présence et en absence d'un agitateur statique. Ces valeurs ont été comparées à celles obtenues dans un réacteur en cuvée. La composition du copolymère dans un réacteur tubulaire pour chaque recette a un comportement unique. L'effet du taux d'écoulement sur la conversion et la vitesse de la réaction a été étudiée. Pour chaque région d'écoulement, la variation de la composition d'acétate de vinyle dans l'alimentation a également un comportement unique. Le type et la forme du réacteur (batch ou continu), ainsi que le taux d'écoulement et l'agitateur statique ont un effet important sur les rapport de réactivité de l'acétate de vinyle et l'acrylate de butyle. Dans les réacteurs tubulaires, la réactivité de deux monomères dépend du taux d'écoulement et de la présence d'un agitateur statique. La vitesse d'écoulement et les compositions du monomère dans l'alimentation ont peu d'effet sur la fraction molaire de l'acétate de vinyle dans le copolymère alterné.

ABSTRACT

Emulsion polymerization is a technologically and commercially important reaction, which grew rapidly in use following intensive research into its application to the production of synthetic alternatives to natural rubber latex during the World War II. Nowadays, emulsion polymerization is the basis of a massive global industry that continues to expand, mainly through the versatility of the reaction and greater realization of the ability to control the properties of the polymer latexes produced. The diversity of applications for emulsion polymerization is evident in the wide range of products that include synthetic rubbers, toughened plastics, paints, adhesives, floor polishes, sealants, cement, concrete additives, and drug-delivery systems.

Emulsion polymerization has been well studied in batch systems and to a lesser extent in continuous stirred tank reactors; however, there has been very little work done with tubular reactors. This is surprising in the light of the potential advantages of such a system.

The main objective of the proposed work is to study the copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. Specific objectives are as follows:

- To establish the best conditions using a tubular reactor with and without a static mixer.
- To evaluate the effect of static mixer on the characteristics of the product, as well as on the particle size distribution in the above mentioned systems.
- To determine the effect of operational parameters on particle size distribution and copolymer composition.

By studying copolymerization of vinyl acetate and butyl acrylate in a tubular reactor different flow regions were found in which conversion is in its maximum. The experimental data obtained show that each monomer composition in feed reaches a maximum in a flow region that is different from the others. Also it was found that the amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. Lower levels of butyl acrylate and the velocity of fluid flowing inside the tube having a strong effect on the shape and the width of particle size distributions. This effect may vary at different levels of butyl acrylate and flow rate. The results obtained from copolymer composition showed that in most experiments an alternating block copolymer is formed during the reaction.

Emulsion copolymerization in presence of static mixer was evaluated by comparing the data obtained from the experiments in presence and in absence of static mixer. It was found that there is a flow region in which the emulsion copolymerization has maximum conversion. This region could be displaced by changing feed composition, and by the presence of a static mixer. A static mixer can change the distribution of particle size in final latex, and has strong effect on the molecular structure of the product.

The apparent reactivity ratio of the vinyl acetate with butyl acrylate were determined at different flow regions and it was compared with the ones determined in a batch reactor, and the ones determined in a tubular reactor equipped with and without a static mixer. It was found that copolymer composition in a tubular reactor for each recipe has a unique behavior that is on from another, as well as those obtained in a batch reactor. Effect of flow rate was investigated on conversion and copolymerization rate. It was found that in each flow region, variation of mole fraction of vinyl acetate in feed has a unique behavior. Type and shape of reactor (batch or continuous), flow rate and presence or absence of a static mixer have strong effect on the apparent reactivity ratios of vinyl acetate and butyl acrylate. In tubular reactors, the reactivity of the two monomers depends on the fluid velocity and the presence of a static mixer. Also it was found that flow rate and feed's monomer compositions have little effect on the mole fraction of vinyl acetate in the copolymer.

CONDENSÉ EN FRANÇAIS

Les procédes en continus sont des altérnatives intéressantes aux procédés en cuvée généralement utilisés. Non seulement les coûts d'opération sont habituellement plus faibles mais aussi, des études fondamentales sur le mécanisme de réaction peuvent être effectuées. Un des premiers procédés en continu fut developpé par le Rubber Reserve Company pour obtenir du caoutchouc synthétique Styrène-Butadiene (SBR) dans les années quarante. Le système était en fait une douzaine de réacteurs reliés en série. Le monomère qui n'avait pas réagi était récupéré et recyclé. La conversion était controlée de façon continue et la composition des réactifs était réajustée continuellement. Plusieurs des procédés SBR développés initialement, sont toujours en operation.

Depuis quarante ans plusieurs procédés en continus ont été adaptés pour une gamme de produits tels que le polychloroprène, l'acétate de polyvinyle, l'acétate de polyéthyle ainsi qu'une série de cautchoucs synthétiques.

Parmi les bénefices les plus importants pour les procédés en réacteurs continus, on peut citer les points suivants:

1. Hauts taux de production, des investisements en capitaux et des coûts d'opération faibles.

2. Produit de qualité constant alors que la qualité peu varier d'une cuvée à l'autre pour les procédés discontinus.

3. La capacité du système de transfert de chaleur est utilisé continuellement à son maximum. Le pic exothermique bien connu peut être négligé contrairement aux procédés en cuvées.

4. Les réacteurs tubulaire sont conçus pour fonctionner complétement remplis avec très peu d'espace vapeur ce que élimine les problémes d'intérface et de coagulation sur les parois.

La polymérisation en émulsion a bien été étudiée avec les systèmes en cuvées et à degré moindre dans les CSTRs (Continuus Stirred Tank Reactor); cependant, il y a eu très peu d'étude ont été effectueés avec des réacteurs tubulaires. Ceci est peu surprenant si on tient compte des avantages potentiels d'un tel système.

Cependant rien n'a été publié sur la copolymerisation en émulsion de l'acétate de vinyle avec de l'acrylate de butyle ni en procédé continu ni en réacteur tubulaire.

L'objectif principal du travail proposé est d'étudier la copolymérisation en 'émulsion de l'acétate de vinyle et de l'acrylate de butyle dans un réacteur tubulaire. Les objectifs spécifiques sont comme suit:

- Établir les meilleures conditions d'opération d'un réacteur tubulaire avec et sans agitateur statique.
- Évaluer l'effet de l'agitateur statique sur les caractéristiques du produit, aussi bien que sur la distribution de la taille des particules dans les systèmes précités.
- Déterminer l'effet de paramètres opérationnels sur la distribution de la taille de particule et la composition du copolymère.

L'émulsifiant est dissout dans 1000mL d'eau distillée avec 10 gouttes de Nopco, un agent antimoussant. L'initiateur a été dissout dans 200mL d'eau distillée. Tout le système y compris le tube, le réservoir de l'émulsion, et le réservoir de l'initiateur, est purgé par de l'azote afin d'éliminer l'air dans la système. La solution d'émulsifiant et les quantités requises d'acétate de vinyle, d'acrylate de butyle ainsi que 1500mL d'eau distillée sont versés à l'intérieur du réservoir de l'émulsion. L'emulsification est éffectuée grace à l'agitateur. L'agitation est poursuivie pendant 50 minutes afin de s'assurer d'une émulsification complète. L'emulsion est alors transferée au réacteur tubulaire et la pompe à mouvemente alternatif est reglée à sa plus haute vitesse afin d'atteindre le plus rapidement possible la température du réacteur, 60°C. Ceci prend habituellement entre 15 et 25 minutes selon les ingrédients présents dans le mélange. Lorsque la température desirée est atteinte, la vitesse de la pompe est ramenée à la vitesse prévue pour obtenir le nombre de Reynolds désiré. L'émulsion est mélangée pendant approximativement 30 minutes afin d'atteindre un profil de vitesse constant. Après cette période, la solution de l'initiateur préchauffée est injecté dans le tube en forçant de l'azote à travers le réservoir de l'initiateur. Ceci est considéré comme le début de la réaction de copolymérisation. La polymérisation prend environ 2 heures. Pendant toute la réaction, les échantillons sont prélevés pour analyses. La réaction dans les échantillons prélevés est stoppeé avec de l'hydroquinone. A la fin de la réaction, la pompe est arretée et le latex est évacué par la valve d'échantillonage. La valve a trois voies est ouverte et tout le système est rincé à l'eau.

Les échantillons prelévés ont été analysés pour la conversion, la distribution de la taille des particules et la composition du copolymére. La distribution de la taille des particules est mesurée à l'aide un appareil de dispersion de lumière laser de Brookhaven Instruments Corporation, couplé à un BIMODAL-203AT à correlation numériques. Pour cette analyse, l'eau doublement distillée et sans poussières a été utilisée. La mesure a été effectueé à 25 °C. Les données obtenues nous ont permis d'établir une distribution basée sur la fraction des grosseurs des particules.

Un Brucker WH400 spectromètre (400.13 MHz) a été utilisé pour obtenir la composition molaire de latex par les spectres RMN. La résonance de groupe CH dans l'acétate de vinyle (5.22 ppm) et la résonance de -O-CH_2 groupe dans acrylate de butyle (4.13 ppm) sont connus, et la composition de copolymère a pu être calculée en mesurant la surface sous chaque pics aux résonances précitées [Bataille et Bourassa (1989)].

Les nombres de Reynolds de 6500, 7500, 8600, et 9700 ont été utilisées pour chaque groupe d'expériences. La pompe à mouvement alternatif a été calibrée avec de l'eau à 60 °C.

Les mêmes expériences ont été répetées dans le réacteur tubulaire équipé d'un agitateur statique.

Les résultats d'expériences avec le réacteur tubulaire sont comparés avec les résultats obtenus avec le réacteur en cuvées de Kong et al (1987).

Cette étude a demontré que la conversion obtenue dans le réacteur tubulaire était plus faible que dans le cas d'un réacteur en cuvée .

Dans tous les cas, des maximums de conversion sont obtenus. L'emplacement et l'amplitude de ces maximums dépendent de la composition de l'alimentation et du taux d'agitation.

Avec 5% pds. d'acrylate de butyle le maximum est dans la région de l'écoulement turbulent avec une conversion d'approximativement 96% pds. Quand la concentration d'acrylate de butyle augmente à 15% wt. deux maximum apparaisent avec, cependant, une baisse dans la conversion à approximativement 67%. Un des points intéressants est le fait qu'un des maximums se produit dans la région de l'écoulement turbulent et l'autre de la region laminaire ce qui suggère deux mécanismes de réaction. Quand le niveau d'acrylate de butyle augmente à 25% pds nous avons un aplatissement de la courbe de conversion mais encore une fois deux pics paraissent un dans la région de l'écoulement du laminaire et l'autre dans la région de l'écoulement turbulent.

En augmentant la quantité d'acrylate de butyle dans l'alimentation on a observé un déplacement des conversions maximales vers la région d'écoulement turbulent. L'acrylate de butyle a un effet négatif sur la conversion finale dans quelques régions et un effet positif dans d'autres régions.

Pour le système d'écoulement transitoire laminaire-turbulent le nombre de particules produit est le plus elevé quand la composition de l'alimentation est à 5% pds l'acrylate de butyle et 95% pds l'acétate de vinyle Loraqu'on augmente la concentration del'acrylate de butyle de 15% pds à 25% pds, généralement, il y a une baisse dans le nombre de particules formées. Dans l'écoulement turbulent, le plus grand quantitéde particules est obtenue avec 15% pds d'acrylate de butyle et 85% pds d'acétate de vinyle après 20 minutes, cependant, l'ordre d'importance du nombre de particules formées revient à celui formé pour l'écoulement transitoire laminaire-turbulent. On a noté que'avec un réacteur tubulaire la quantité d'acrylate de butyle dans le système a un effet direct sur le nombre de particules produites et sur la conversion finale.

L'évolution de distribution de la taille de particule est analysée continuellement pendant toute la réaction. Une nucléation secondaire est observée ainsi qu'une distribution bimodale, tôt dans la polymérisation.

L'existence de nucleation secondaire confirme cela qu'il y a lieu une nucleation homogène pendant le copolymérisation du a la solubilité d'acétate de vinyle dans l'eau [Kong et al. (1988)].

La distribution de la taille des particules du latex pendant la réaction avec 95 wt% acétate de vinyle et 5 % pds l'acrylate de butyle est large et bimodale. Cependant la distribution de la taille de particule du produit du latex de 85 % pds acétate de vinyle, 15 % pds acrylate de butyle, et 75 % pds d'acétate de vinyle, 25 % pds d'acrylate de butyle est étroite et monomodale. Dans la réaction avec 85 % pds d'acétate de vinyle, il y a toujours deux régions d'écoulement différentes où une distribution de la taille des particules est monomodale, mais la distribution de la taille des particules obtenues avec l'écoulement très turbulent est plus étroite que la distribution de la taille des particules obtenues avec l'écoulement transitoire laminaire-turbulent.

Dans le cas de 75 % pds d'acétate de vinyle, les deux distributions de la taille des particules sont également monomodales alors que la distribution obtenue avec l'écoulement laminaire est plus étroite que celui obtenu avec un écoulement turbulent.

Généralement, la copolymérisation en émulsion d'acétate de vinyle et de l'acrylate de butyle dans le réacteur tubulaire est très contrastante a comparer aux les résultats obtenus par Kong et al (1987) avec un réacteur en cuvée ou avec des réacteurs semi-continus. Lorsqu'ils augmentaient la quantité d'acrylate de butyle dans l'alimentation une distribution de taille des particules plus étroite est obtenue. Nous avons trouvé que la quantité d'acrylate de butyle et la vitesse de l'écoulement ont des effets importants sur la forme (monomodale-bimodale) et sur la distribution de la taille des particules. De plus, la composition chimique de l'alimentation, le taux de l'écoulement a aussi un effet dominant sur les propriétés du latex y compris distribution de la taille de particule et la taille moyenne de la particule.

La composition du copolymére a été mesurée tout au cours de la polymérisation par RMN.

En tenant compte des rapports de réactivité de l'acétate de vinyle (r_1=0.024) et de l'acrylate de butyle (r_2=10.67) [Bataille et Bourassa (1989)] il est suggèrer que le polymère serait constitué de deux longues chaînes d'acétate de vinyle, et d'acrylate de butyle relié ensemble, c.-à-d. un copolymère bloc. Cependant la quantité d'acétate de vinyle dans le copolymère peut varier ce qui explique la formation d'un copolymère altterné bloc. La composition instantanée du copolymère a été calculée à partir des données RMN pour confirmer cette idée. La composition instantanée du copolymère est définie comme la proportion molaire d'acétate de vinyle (donneur d'électron) à l'acrylate de butyle (accepteur d'électron) dans le copolymère [Cowie (1989)].

Si la composition instantanée du copolymère est entre 1 et 2 le latex est un copolymère parfaitment alterné, et s'il dépasse 2 nous avons un copolymère bloc alterné. On a observé qu'au cours de la réaction la composition instantanée du copolymère augmente. On croit que la réactivité des monomères varie pendant la réaction. Finalement un latex avec une structure de bloc alterné est obtenu. En d'autres termes dans un réacteur tubulaire il est possible de diminuer la variation de la composition et d'éviter de grandes variations de la composition qui existe par de la copolymérisation dans un réacteur en cuvée [Kong et al. (1987)].

Deux groupes d'expériences ont été effectueés en présence et en absence d'un agitateur statique pour évaluer l'effet d'un agitateur statique sur la réaction. On a observé qu'avec 5 % pds d'acrylate de butyle et 95% pds d'acétate de vinyle atteint son maximum tôt dans l'écoulement turbulent (Re=8600).

A des nombres de Reynolds moins que à 8600, à cause du risque de séparation de phase et de la coagulation des particules, des conversion faibles ont été obtenues. Pour des nombre de Reynolds plus élvés que 8600, la coagulation est la cause principale des faible conversions. Ceci confirme les résultats obtenues par Lynch et Kiparissides (1981). Les réactions qui contiennent 15% pds d'acrylate de butyle et 85% pds d'acétate de vinyle ont un comportement sinusoidal. Dans la région de l'écoulement laminaire (Re=6500) la conversion est 51.4 % pds. La conversion dans l'écoulement transitoire laminaire-turbulent (Re=7500) augmente à 57.8 % pds.

Au début de l'écoulement turbulent, encore une fois, il y a diminution de la conversion à 51.1% pds, et finalement, dans l'écoulement très turbulent (Re=9700) la conversion augmente à 59.0% pds.

Généralement, on peut dire que la coagulation a un effet important sur la copolymérisation en émulsion dans un réacteur tubulaire et limite la conversion à 59.0 %pds. Cet effet est amplifié dans quelques régions.

Les copolymérisations en émulsion qui contiennent 25% pds d'acrylate de butyle et 75% pds d'acétate de vinyle ont, aussi, un comportement du sinusoidal qui est exactement le meme que dans le cas décrit précédemment. L'effet de la coagulation est plus dominant et la conversion finale est limitée à 67.9% pds dans l'écoulement laminaire.

Dans tous les cas, la coagulation cause une réduction dans le nombre de particules du polymère, et finalement une réduction dans le taux de copolymérisation en émulsion. Il devrait être noté que dans la région d'écoulement laminaire, il y aussi séparation de phase dans le cas avec 5 % pds d'acrylate de butyle et 95 % pds d'acétate de vinyle, ce qui limite l'efficacité de la copolymérisation en émulsion.

Dans la réaction avec un agitateur statique il a été observé qu'à l'exception du cas de 95 % pds d'acétate de vinyle et 5% pds d'acrylate de butyle dans l'alimentation, le comportement dans tous les cas est semblable. La courbe est similaire avec la réaction a 85 % pds d'acétate de vinyle cela avec une augmentation du nombre de Reynolds (ou taux de l'écoulement) la conversion finale s'améliore et avec un écoulement très turbulent (Re=9700) et atteint son maximum (79.4% pds).

La conversion est en rapport direct avec l'alimentation qui contient 15% pds d'acrylate de butyle et a un comportement du sinusoidal. Dans la région laminaire, la conversion atteint 42.4% pds.

Dans l'écoulement transitoire laminaire-turbulent, la conversion augmente à 67.3 % pds alors que dans la région de l'écoulement turbulent, il diminue à 51.8% pds.

En augmentant le nombre de Reynolds dans la région de l'écoulement très turbulent, la conversion atteint 62.2 % pds.

Dans le cas de 75 % pds d'acétate de vinyle, un comportement sinusoidal est aussi obsevé. Dans la région de l'écoulement laminaire la conversion est 43.1 % pds, la conversion augmente dans la région de l'écoulement laminaire-turbulent à 58.7 % pds, et baisse ensuite à 51.7 % pds dans la région de l'écoulement turbulent. Finalement il augmente encore une fois et atteint 65.16 % pds dans l'écoulement très turbulent qui est la conversion maximale obtenue.

Généralement la présence de l'agitateur statique exerce un cisaillement sur les particules et ce cisaillement les déstabilisera, la coagulation a aussi un effet majeur sur la valeur de conversion maximale dans toutes les expériences. Ce cisaillement ainsi que la coagulation diminue la conversion finale. Dans tous les cas, la coagulation cause une baisse du nombre de particules polymère et affecte l'évolution de la réaction. Il doit être noté que dans la région d'écoulement laminaire dans le cas d'une alimentation qui contient 5 % pds d' acrylate de butyle, la séparation de phase affecte la vitesse de la réaction et la conversion.

L'évolution de la distribution de la taille des particules a été déterminée pour toutes les expériences. Pour les réactions en l'absence d'un agitateur statique pour 5 % pds d'acrylate de butyle dans l'alimentation la conversion maximale est de 95.7 % pds.

Dans la région de l'écoulement turbulent (Re=8600) on a initialement une distribution de la taille des particules trimodale et large. La distribution devient monomodale et étroite après 30 minutes. La forme générale de cette distribution ne change pas pendant le reste de la réaction. À la fin de la copolymérisation en émulsion une nucleation secondaire cause un changement de la distribution qui devient bimodale. Généralement dans cette région de l'écoulement le nombre de micelles produites en début de réaction est très élevé et empêche la nucléation secondaire pendant la réaction obtient un latex avec des particules variant entre 45 et 438 (nm).

La présence d'un agitateur statique a permis d'obtenir dans la région d'écoulement très turbulent (Re=9700) une conversion maximale de 79.4 % pds.

Après 10 minutes, la distribution de la taille des particules est monomodale et après 20 minutes et 50 minutes la courbe est d'abord bimodale et ensuite monomodale. Pendant la réaction il n'y a essentiellement aucun changement dans la taille et la distribution des particules et c'est seulement à la fin de la réaction que la dernière courbe PSD devient bimodale avec une distribution plus large. Au début de la réaction, un nombre maximale de particules actives sont formés et la nucleation secondaire est ramenée à son niveau minimum. C'est pourquoi que les courbes PSD restent monomodales presque jusqu'à la fin de la réaction. À cause de la presence d'un agitateur statique, le cisaillement est appliqué aux particules, les détruisent et le flocculation se produit. Le flocculation provoque une augmentation dans la taille de particules et change la distribution monomodale en une distribution bimodale. Le latex est constitué de particules dans une plage de taille de particules entre 74 et 1000 nm.

Le réaction en l'absence d'un agitateur statique avec 15 % pds d'acrylate de butyle dans alimentation, ramène la conversion maximale a 59.04 % pds.

Dans la région de l'écoulement très turbulent (Re=9700), il a été observé que la copolymérisation en émulsion commence avec une distribution de la taille des particules bimodale et y reste pendent les 50 premières minutes. Une fois cela passé la distribution devient monomodale jusqu'à la fin de la réaction. Avec une distribution de la taille des particules étroite de 50 à 230 nm, la nucleation est complétée tôt dans la réaction. Il n'y a aucune nucléation secondaire observée pendant la seconde partie de la réaction.

La présence d'un agitateur statique avec un écoulement laminaire-turbulent (Re=7500) la conversion maximale est portée a 67.3 % pds. La copolymérisation en émulsion commence avec une distribution de la taille des particules bimodale. Durant l'évolution de la copolymérisation en émulsion, un système monomodale est adopté jusqu'à la fin de la réaction. Il y a une petite tendance vers la formation de plus petites particules pendant la réaction pendent les 80 premières minutes de la réaction après que la distribution de la taille des particules devienne plus étroite et monomodale, avec une base plus large. La distribution finale de la taille des particules est monomodale, et large (38-306 nm).

À cause de l'augmentation de la quantité d'acrylate de butyle dans l'émulsion, la variation de la grandeur des particules diminue et la nucléation secondaire est à un minimum.

Les résultats de 25% pds sont semblables ceux obtenus avec 15% pds d'acrylate de butyle dans l'alimentation.

La composition de la copolymère instantanée (m) est définie comme le rapport molaire entre l'acétate de vinyle (donneur d'électron) et l'acrylate de butyle (accepteur d'électron) polymérisé sur le copolymère en criossance effectué dans un certain lapse de temps. Il faut noter qu'il y a deux types de copolymères: le premier type contient des montants égaux de donneurs d'électrons et d'accepteur d'électrons (m=1), avec la deuxième type la quantité de donneur d'électron est deux fois plus elevée que les acceptateur d'électrons (m=2)

Dans le cas ou (m) est plus grand que 2, le copolymère résultant est un copolymère en bloc alterné [Cowie (1989)].

En l'absence d'agitateur statique on a trouvé, avec 95 % pds d'acétate de vinyle dans l'alimentation, la composition du copolymère instantanée a un maximum dans l'écoulement turbulent. Le produit dans l'écoulement laminaire est riche en acrylate de butyle et pauvre en acétate de vinyle. Avec les écoulements laminaire-turbulent, turbulent, et très turbulent le produit est un copolymère bloc alterné avec variation dans la longueur des séquences d'acétate de vinyle. Avec une alimentation 85% pds d'acétate de vinyle, le taux de l'écoulement a moins d'effets sur composition instantanée du copolymère. Le produit est un copolymère bloc alterné avec des chaînes de vinyle plus petit que dans les cas antérieurs. Avec une alimentation 75% pds d'acétate de vinyle, le taux d'écoulement a moins d'effets que dans les cas précédents sur la variation de la composition instantanée du copolymère. Ici, les produits sont surtout des copolymères alternée.

En présence de l'agitateur statique et avec une alimentation contenant95% pds d'acétate de vinyle, la composition instantanée du copolymère a un comportement sinusoidal. Il commence à augmenter avec l'écoulement laminaire et est porté à un maximum dans la région de l'écoulement laminaire-turbulent et il diminue ensuite avec l'écoulement turbulent, pour augmenter de nouveau dans l'écoulement très-turbulent. Dans toutes les régions le copolymère final est un bloc alterné qui a des longeurs différerante de blocs d'acétate de vinyle, mais dans la plupart des cas ils sont plus petites que ceux produits en l'absence de l'agitateur statique. Avec 85 % pds d'acétate de vinyle dans l'alimentation, la composition instantanée du copolymère a un maximum dans l'écoulement turbulent. Dans l'écoulement laminaire et l'écoulement très-turbulent, le produit est un copolymère alterné, et dans l'écoulement transitoire laminaire-turbulent et la région d'écoulement turbulent, un copolymère bloc alterné est formé. Avec 75 % pds d'acétate de vinyle, la composition instantanée du copolymère a un comportement sinusoidal limité. Dans toutes les régions le copolymère est alterné.

Généralement avec l'augmentation de la quantité d'acrylate de butyle dans l'alimentation, les séquences d'acétate de vinyle deviennent plus petites et la structure du copolymère a tendance à devenir alternée plutôt qu'en blocs alternés.

Les rapports de réactivité apparents ont un comportement unique pour le réacteur tubulaire a comparer avec ceux obtenu dans un réacteur en cuvée. Un azéotrope a été observé dans l'écoulement transitoire laminaire-turbulent. Type et forme de réacteur (cuvée ou continu), et le taux découlement ont un effet important sur les réactivités respectives des monomères. La variation de la composition des copolymère est aussi une fonction de ces paramètres. Les rapports de réactivité, r_1 et r_2 ont des valeurs différentes dans les conditions d'écoulement différentes. Cela veut dire que la réactivité des deux monomeres dépend de la nature des monomères, et du taux d'écoulement. En ajustant l'écoulement on peut obtenir un copolymère avec une structure spécifique. L'agitateur statique peut réduire la variation de la composition, à comparer avec les resultats obtenus avec le réacteur en cuvée. Cependant, il a un effet majeur sur la polymérisation car il réduit la réactivité apparente de l'acétate de vinyle dans l'écoulement laminaire, l'écoulement transitoire laminaire-turbulent, et l'écoulement turbulent, et il l'augmente avec un écoulement très-turbulent. Aussi, le taux d'écoulement et la composition du monomère dans alimentation, a un effet sur la fraction molaire d'acétate de vinyle dans le copolymère.

Ce travail a permis de dégager les points suivantes. Dans un réacteur tubulaire, il y a des régions d'écoulement différentes dans lequelles la conversion obtenue peut être maximale. La quantité d'acrylate de butyle a un effet important sur le nombre des particules et sur la conversion finale. Les résultats obtenus pour la composition du copolymère ont montré que dans la plupart des expériences, un copolymère bloc alterné est obtenu. Avec la copolymerization en émulsion et en présence d'un agitateur statique on a trouvé que la valeurs des conversions maximales diminuent. La région de conversion maximale se déplace, et ce déplacement dépend de la composition de l'alimentation. L'agitateur statique peut changer aussi la distribution des particules dans le latex finale, et a aussi un effet important sur la structure moléculaire du produit. La composition de copolymère dans un réacteur tubulaire a un comportement spécifique pour chaque recette. Dans les réacteurs tubulaires, la réactivité de deux monomères dépend du taux d'écoulement et de la présence d'un agitateur statique.

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F_1: Mole fraction of vinyl acetate in copolymer added to the polymer at time t

f_1: Mole fraction of vinyl acetate in feed

f_2: Mole fraction of butyl acrylate in feed

r_1: Reactivity ratio of vinyl acetate

r_2: Reactivity ratio of butyl acrylate

m: Instantaneous copolymer composition

CHAPTER 1 : INTRODUCTION

1.1 Introduction

Emulsion polymerization is a widely used process for the production of polymers. The product latex, a submicron suspension of colloidally stable polymer particles in an (usually) aqueous medium , has many desirable properties. The low viscosity of the latex reduces pumping and agitation equipment loads and improves heat transfer to the reactor walls. The heterogeneous nature of the process enables the simultaneous achievement of high molecular weight and high reaction rates. Latexes have desirable film forming properties depending on the monomer used which warrant the use of emulsion polymerization whenever the final product is to be used in a coating application. Lastly, environmental concerns call for an increasing use of aqueous based products for architectural and structural coatings.

To acquaint the reader with some of the time and length scales that occur in emulsion polymerization, a typical batch polymerization is described here. The description is based on an early analysis of the process by Harkins (1947).

Figure 1-1 shows the constituents of an emulsion polymerization reaction. Initially, the ingredients are water (or some other suspending medium), monomer, aqueous phase soluble initiator, and an emulsifier (surfactant or soap). Monomer is present in quantities of 10-50% by volume. Most monomers are only partially soluble in the aqueous phase (0.27 g/l for styrene [Coulter (1970)], 15.6 g/l for methyl methacrylate [Luskin (1970)], and 23.4 g/l for vinyl acetate [Leonard (1970)]. The bulk of the monomer is present in drops 10μ in diameter formed by agitation. Some of the surfactant adsorbs on the surface of the monomer drops. The remaining surfactant resides in the aqueous phase.

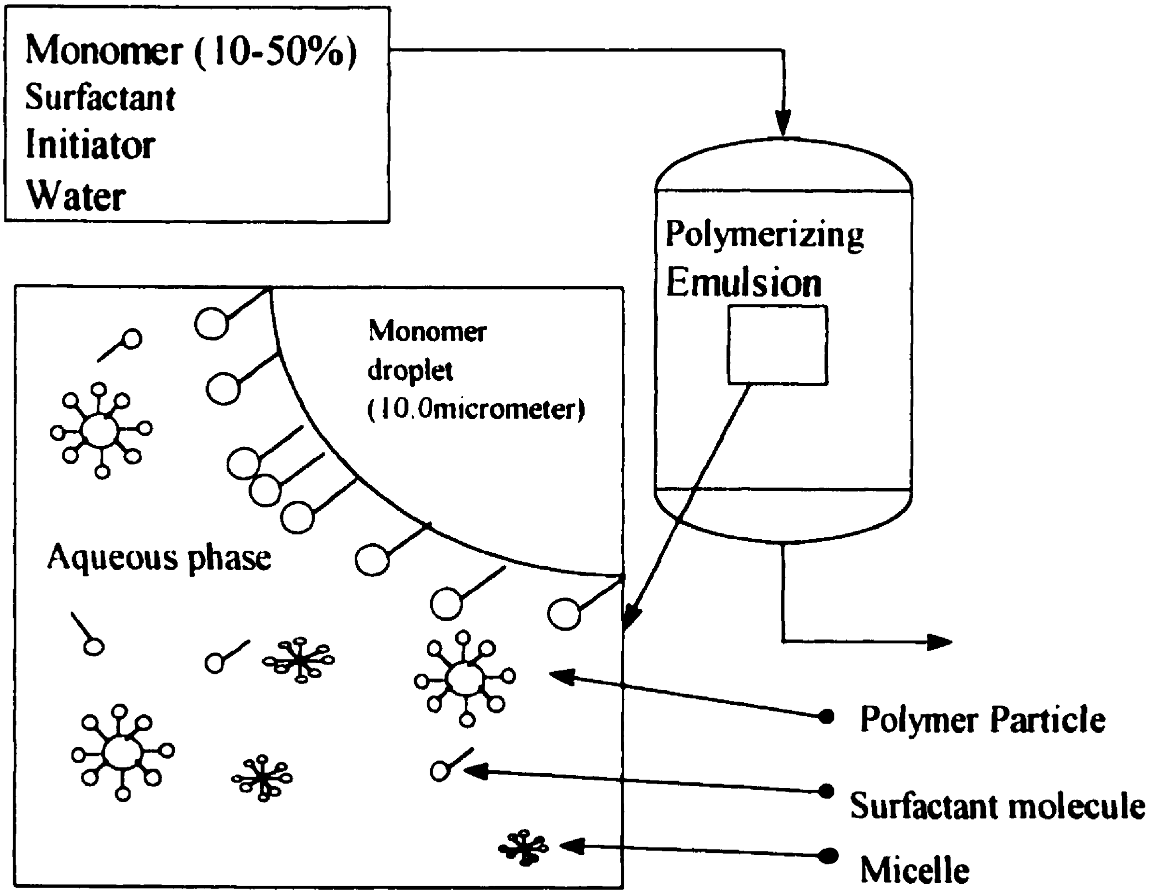

Figure1-1: Emulsion polymerization

Typically the concentration of surfactant in the aqueous in above its critical micelle concentration (CMC) [1] and forms micelles. The centers of the micelles are hydrophobic

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[1] The CMC is the concentration above which surfactant aggregates or form micelles.

and some monomer enters and swells the micelles. The micelles serve as particle nucleation sites and surfactant reservoirs for growing particles.

Particle nucleation occurs when an aqueous phase free radical, formed by initiator decomposition, enters a monomer-swollen micelle and polymerizes. As the reaction proceeds, monomer is supplied to the particles from the monomer droplets and maintains the monomer concentration in the particles. Thus, the number of micelles will eventually disappear due to nucleation and growth of the particles. Nucleation (interval I in Harkins description) ceases when the micelles disappear; the aqueous phase concentration is at its CMC and the rest of the surfactant is adsorbed on the particles. For batch systems, the nucleation period ends at low values of conversion (< 10%) and is characterized by an increasing particle number. The final particle number is approximately 3 orders of magnitude less than the initial micelle number.

The reaction proceeds at a nearly constant rate during interval II (polymerization in the presence of monomer dropletss). The fixed rate is due to a constant number of polymer particles and a constant monomer concentration in the particles. The presence of the monomer droplet phase ensures a saturated monomer concentration in the particles. The small monomer drops have sufficient area for a negligible mass transfer resistance to the particles. Polymerization continues as radicals enter, desorb and terminate within the particles. The interval ends when the monomer droplets or reservoirs are consumed. Thermodynamic equilibrium between the aqueous phase and the polymer particulate phase determines the conversion at which the drops disappear (40% for styrene, 27% for methyl methacrylate, and 15% for vinyl acetate).

The final stage (interval III) of the reaction proceeds with a continuously decreasing monomer concentration. Only the particles and aqueous phases exist and agitation is needed only for heat transfer. For some systems (notably styrene and methyl methacrylate), due to the existence of monomer inside the polymer-monomer particles the reaction rate does not decrease with the depleting monomer and it overshots the expected decrease in reaction rate. The lower monomer concentration is offset by an increasing radical concentration due to the termination gel effect. The gel effect occurs when the termination rate constant decreases because of the reduced mobility (due to the decreasing monomer concentration) of the growing oligomers. Methyl methacrylate also demonstrates a propagation gel effect in which monomer transport is hindered. For this system, the reaction ceases at conversions less than 100%.

In batch reactors, the three intervals occur in sequence: nucleation, growth with drops, growth without drops. A narrow particle size distribution forms since the nucleation interval happens over a short period. The low concentrations at which the micelles disappear give rise to the final particles that are only partially protected by surfactant. The average final particle diameter is typically 100 nm.

Economics favor a continuous process over a batch system when product volumes are large enough or when product grades differ slightly. A continuous process also offers improved quality by eliminating batch to batch variations. A continuous stirred tank reactor (CSTR) and a tubular reactor are two potential candidates for such a process. Emulsion polymerization in a CSTR offers several challenges. Steady state multiplicity occurs due to the termination effect. In addition, the steady state is often unstable. Experimental and theoretical studies have confirmed the presence of sustained oscillations in conversion over a wide range of conditions. Rawlings and Ray (1987) concluded that the small particle growth rate determined the reactor's stability. Monomers with high radical desorption (and hence low small particle growth rate) are more likely to produce oscillations. Oscillatory behavior should be avoided, as varying product quality varies which is not acceptable.

Some systems (styrene) have stable steady states. In stable CSTRs, nucleation and growth occur simultaneously. For nucleation, the micelles must be present and thus the particles must be completely covered by surfactant. For equivalent polymer productivity, the total particle number is less than that in a batch reactor. The lower particle number is compensated by a greater average particle size. In addition, the experimental residence time distribution of a CSTR produces a broad particle size distribution. The particle size influences the number of radicals in the particle and hence the molecular weight of the polymer produced. The broad particle size distribution may produce a molecular weight distribution that is different from that of the batch system. Also, the film forming properties of latex are dependent on its particle size distribution. Because the broad PSD may have different properties than the batch latex, the CSTR cannot be used in a continuous process to replace the batch system.

A tubular reactor appears to be a suitable alternative of the CSTR as a continuous process. The large surface area of the tube is particularly advantageous for the strongly exothermic polymerizations. The narrow residence time distribution, indicates that a tubular reactor will produce latex with a narrow particle size distribution. Stable operation is also expected from a tube with its greatly reduced backmixing. Unfortunately, the plugging of the reactor can overwhelm these advantages. This phenomenon occurrs when the latex becomes unstable. At that time particles agglomerate and the reactor will be plugged.

1.2 Background

Emulsion polymerization has been well studied in batch systems and to a lesser extent in CSTRs; however, there has been very little work done with tubular reactors. This is surprising in the light of potential advantages of such a system. A review of the reported work in tubular emulsion polymerization is presented below.

1.2.1. Loop Reactors

Rollin et al.(1977) studied the influence of the Reynolds number on the rate of polymerization of styrene in a closed-loop reactor. Using the same recipe(styrene/water : ¼ by volume; potassium persulfate 3.19×10^{-3} moles/l-aq; sodium lauryl sulfate 8.15×10^{-3} moles/l-aq; and a temperature of 60°C),they varied the Reynolds number (based on the initial conditions) from 415 to 13600. The reactor was a 7.7mm ID stainless steel tubing 18.9 meters long and was shaped in a loop with straight sections jacketed by a 20 mm ID copper tubing to maintain isothermal conditions. At one end of the loop there was a screw-type pump for recirculation. The reactor was operated in a closed loop batch mode. An experiment started with the reactor charged with monomer, surfactant and water. An emulsion was formed by circulating at Re = 13600 for 30 minutes. Initiator was injected for one residence time, then the flow rate was adjusted to the desired rate and the polymerization proceeded. Samples were taken periodically for conversion analysis(dry solid). A compensation chamber was in the loop to account for the contraction upon polymerization and volume loss due to sampling. Plugging occurred in two of the ten runs reported. During these two runs (Re = 13600) plugging occurred due to poor emulsification; they circulated the emulsion for only 5 minutes prior to injecting initiator. Rollin et al (1977) consistently found a limiting conversion below the final conversion obtained in a comparative batch reactor. Their results showed a maximum in the rate of polymerization and in the value of the limiting conversion when the flow was in the transitions of the monomer. Inefficiencies in tubular flow were thought to be due to a low micelle concentration. They believed that turbulent flow produced smaller drops which adsorbed more surfactant. With more surfactant going to the drops, fewer micelles and particles were formed.

Lynch and Kiparissides (1981) simulated the turbulent experiments of Rollin et al(1977). Their monodisperse model included axial dispersion of initiator it was found that it contributed negligibly to the initiator concentration, micellar nucleation, and particle loss by coalescence. By varying the coalescence rate constant with the Reynolds number, they obtained excellent agreement between model and experimental conversion data.

Bataille and Dalpé (1989) studied the polymerization of vinyl acetate in a closed loop reactor at 60°C.The reactor consisted of four glass tubes of 1.9 cm ID. Two of the tubes were 3 meters long and the other two were 1 meter long. They used a pump similar to the one used by Rollin et al (1977). In the results reported, limiting conversions (50 to 60%) occurred for all cases. Studying Reynolds numbers 4300-8600, they also found an optimum recirculation rate.

Lanthier (1970) in his patent described a continuous loop recycle reactor in which the recycle loop flow rate was much greater than the reactor feed flow rate. This reactor behaved like a CSTR and had the advantage of a large heat transfer area. The patent established the feasibility of a reactor fabricated of aluminum tubing 1cm OD with a loop length of 3-4 meters in the polymerization of vinyl acetate. A typical recipe had a residence time of 7 minutes at 40 °C with a redox initiator. The product latex had a 97% conversion, with approximately 52% solid content. The particles had a diameter of 0.3μm and the latex had a viscosity of 0.28 poise.

Lee et al. (1990) investigated the polymerization of styrene in a continuous loop recycle reactor. The reactor consisted of a four glass tubes of 4.6 cm ID. The vertical tubes were 46cm in length and the horizontal tubes were 32 cm in length. A blade impeller in one of the vertical tubes was used for recirculation. With recirculation rates much larger than the reactor feed rate, they found the reactor operated like a CSTR.

Bataille and labbadène (1994) studied the emulsion polymerization of vinyl acetate in a loop reactor. They did their experiments in a 5m Teflon tube surrounded by a stainless steel mesh 1m diameter coiled, placed in a thermostated bath, equipped with a reciprocating pump. It had a glassy section to visualize the reaction. They compared their results with that the ones obtained with 1l batch reactor. They also, examined the effect of silver ion on reducing the reaction time . The products were tested gravimetrically for reaction yield, GPC for molecular weight distribution and average molecular weight, and scanning electron microscope and image analyzer to find particle size distribution and the average particle size.

In that work it was found that agitation or flow rate had an important effect on the vinyl acetate polymerization. They worked over Re = 3500 - 10500. The optimum conversion occurred in a narrow zone between Re = 5500 - 8500. Preselection of particle size was possible by variation of flow rate and reaction time. Presence of silver ions ($AgNO_3$) reduced reaction time from 100 min. to 80 min. to reach the maximum conversion. Emulsifier concentration had an effect on concentration and particle size.

1.2.2. Seed Reactor

Ueda et al. (1971) used a plug flow reactor (PFR) to produce seed particles for a CSTR. They compared the number of particles formed in a tubular seed reactor with the quantity formed in a batch reactor. The PFR produced fewer particles and thus a lower rate of reaction. They attributed this to impurities in the feed system In particular, they stated that it may be difficult to remove dissolved oxygen in a PFR. The reaction system studied was styrene/ water (¼ by volume) at 60°C, with potassium persulfate as initiator 2.55×10^{-3} M, and sodium oleate of 6.17×10^{-3} M. They reported conversion versus time. Particle numbers were calculated based on Smith-Ewart case II kinetics.

Lee and Poehlein (1986) used a fluoropolymer tube as a seed reactor for a CSTR. The seed reactor was 3.18mm ID tubing. By introducing nitrogen plugs to control the residence time, the reactor operated as a plug flow reactor. Limiting the conversion to less than 10% to ensure that no nucleation occurred in the subsequent CSTR, they found that the tubular reactor to operate identically to a batch reactor.

1.2.3. High Conversion Reactors

One of the earliest reported studies in tubes was by Feldon (1955) et al. For the polymerization of GR-S rubber. They cited that a tubular emulsion polymerization had long been considered as a reliable reactor for quality and economic reasons. Several patents discuss such a process in which turbulent flow is induced by adding baffles to the reactor. Most of these attempts failed due to coagulation problems.

Feldon et al (1955) investigated a laminar flow reactor. The reactor was 20 gauge stainless steel tubing 116 cm × 1.58 cm ID in successive 2.69 m straight sections connected by small "U" sections. The reactor was submerged in a tank to maintain isothermal operation at 50°C. they studied a 2/1: aqueous/organic polymerization of styrene (25%) and butadiene (75%). After producing approximately 700kg of polymer (45 days of operation), they concluded from reactor volume measurements that there had been no build-up of polymer in the reactor. They did not report conversion-length data or particle size data. They operated in the laminar flow regime with a Reynolds number (based on the inlet conditions) of less than 1000. Two of the patents they cited highlight one issue prevalent in the use of a tubular reactor. Mark (1939) used turbulent flow in the polymerization of methyl methacrylate. Calcott and Starkweather (1946) claims that the earlier patent produces coagulum when polymerizing "soft" latexes such as isoprene and suggests that laminar flow eliminates this problem.

Ghosh and Forsyth (1976) studied a tubular reactor for polystyrene. The reactor was 1.27 cm ID 316 stainless steel 73.2 m long in a helical coil configuration. They investigated the laminar flow regime (Re from 100 to 1000 based on inlet conditions). They varied the concentration of soap, initiator, and temperature. Reactor plugging occurred, especially at high temperatures (>70°C) and low soap concentrations (< 0.014 M). The thermocouples contributed to the reactor plugging. Intense agitation of the emulsion feed reduced plugging. They reported conversion versus residence time data. Results of electron microscopy for two samples suggested a uniform latex of 0.1 μm diameter.

In addition to their experimental work, Gosh and Forsyth (1976) formulated a model. The model assumed laminar flow with radial dispersion. Also, a monodisperse particle size distribution was used. The reaction rate was calculated using Smith-Ewart case II kinetics with the particle number as a parameter in the model.

Vatanatham and Forsyth (1979) studied emulsion copolymerization in a tube. They used a 6.35mm ID 316 stainless steel reactor 57 meters long. Homopolymerization experiments were performed with styrene, and copolymerization experiments of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS). Some plugging occurred at low soap concentrations and high initiator concentrations. They reported operating conditions in which coagulum did not form. They studied the laminar flow regime (Re from 300 to1000 based on the inlet conditions). Particle size data for the tubular reactor (obtained from electron microscopy) suggested that the particle size distribution is only slightly broader in

reactor length did not permit the investigating of limiting conversion at Re> 1400. Plugging didn't occur in any of the fifteen runs presented. Three experiments had temperature deviations of more than 5°C. Steady state was reached after two residence times.

Studies of Bataille et al. (1985) involved the copolymerization of styrene and α-methylstyrene in the 155.7-meter reactor. The copolymerization results were similar to the homopolymerization results mentioned above: maximum rate at the transition from laminar to turbulent flow

Two German patent applications suggest the use of a tubular reactor for emulsion polymerization. The first German patent application Sutterlin et al. (1982) focuses on the material type for the reactor. Whereas both a stainless steel reactor and a poly(vinylchloride) reactor plugged, polyolefin or fluoropolymer reactors were operated without producing any coagulum. In the several examples described for acrylic monomer polymerization, the latex product was 30% solids with a narrow particle size distribution. The second patent application Sutterlin et al. (1983) specifies the use of a tubular reactor as a finishing reactor for reacting residual monomer. Exploiting the greater heat transfer area, the patent reports a lower residual monomer content of a tubular finishing reactor as compared to a CSTR reactor with the same residence time.

Shoaf and Poehlein (1988) studied the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR and tubular reactors. Tubes of different inside diameters (1/8"-3/16") were used. One set of experiments involved injecting nitrogen plugs into a 1/8" ID tube to achieve plug flow and reduce backmixing. For these experiments, 85% conversion was achieved. The nitrogen flow was difficult to control because of the heating and expansion of the gas. Another set of experiments was performed in a small tube without nitrogen injection. At 70°C and a residence time of 20.9 minutes, the reactor effluent had a 100% conversion. They also obtained complete conversion at 55°C but at a lower flow rates. The average particle size approximately 140nm was similar to that produced in a batch reactor. However, they report phase separation and plugging for some of the experiments at the low flow rates. To eliminate the plugging, they increased the flow rate and added a larger diameter tube to the end of the smaller tube. The conversion of the latex entering the larger diameter tube was high enough to eliminate plugging altogether. Complete conversion was achieved with results similar to a batch reactor. They report exit conversion for various tube lengths. From these studies they discuss scale up to a commercial system.

Paquet et al. (1994) studied emulsion polymerization in a pulsed tubular reactor. They performed their experiments in batch, CSTR, closed loop and a pulsed open loop tubular reactor. In batch process, they used a 1l glass vessel with an external jacket for heating and cooling. Moreover, four removable baffles of 316 stainless steel were used. Temperature was controlled with both a heating and cooling source. They used methyl methacrylate as monomer , Sodium dodecyl sulfate (SDS) as emulsifier and potassium persulfate as initiator. Samples were taken during the reaction and tested for monomer conversion (dry solid) and particle size measurement (light scattering and electron microscopy). Also they used an online densimeter at 25°C to obtain conversion data. The reaction was completed in one hour.

Experiments in a closed loop reactor were done in a 1.13 cm ID 316 stainless steel tubing which had two sections: a 1880 cm long and coiled in 50 cm loops, placed in water bath and a 440 cm long connected to a pump and a compensation chamber. They performed the experiments in Re =600 - 13000 and 60°C. In the case of styrene they reported limiting conversions but for methyl methacrylate all the reactions achieved a high conversion.

Experiments in a pulsed tubular reactor was done in 0.533 cm ID by 8794 cm coiled in 50 cm loops. The locations of sampling valves were at 0, 6.3, 16.3, 32.0, 54.6 and 100 % of the tube length. They also used a pulsation source to prevent plugging inside the tube.

Experiments in CSTR was done in 0.5 l glass jacketed reactor with a temperature control. The results of experiments showed that in the open loop reactor plugging occurred and after adding a pulsation source it was eliminated. At low residence times, monomer conversion in a CSTR was low and oscillatory. Conversion was much higher in batch and tube reactors. At higher residence times, the conversion was the same for all three reactors. The average particle size distribution obtained from CSTR latex was twice as large as those obtained in the batch and tubular reactors. Conversion were somewhat higher in batch experiments than in the tubular experiments. The average particle size distribution determined by light scattering were similar for batch and tube. Distributions obtained by scanning electron microscope showed a slight broadening and shift to higher mean size for the tubular latex. Finally, their studies lead to the fact that a pulsed tubular reactor offers superior performance over a CSTR and represents a continuous alternative to the batch reactor.

1.2.4. Other Reactor Types

Hoedmakers (1990) used a pulsed-packed column for continuous styrene emulsion polymerization. The amount of axial dispersion could be varied by adjusting the rate of pulsing. He reported conversion and particle size data along the column for several operating conditions. A steady state axial dispersion model and a series of CSTRs model using Smith-Ewart case II kinetics were developed.

1.3. Objectives

The main objective of the proposed work is to study the copolymerization of vinyl acetate-butyl acrylate in a tubular reactor. Nothing has ben covered out for such a system.

The main objectives are as follows:

- To establish the best conditions using a tubular reactor with and without a static mixer

- to evaluate the effect of static mixer on the characteristics of the product as well as on the particle size distribution in the above systems..
- to determine the effect of operational parameters on the conversion, particle size distribution and copolymer composition.

1.4. Thesis Structure

This thesis is made up of three papers. Besides these papers , which are forming the main body of the thesis as form of different chapters, there are a general introduction, general conclusion, recommendations and six appendices. The content of each part is described below:

- Chapter I consists of a general introduction presenting the global scope of the work and the related features reported in the literature. The objectives of the present studies also outlined.
- Chapter II consists of a conference paper presented in 47th Canadian Chemical Engineering conference in Edmonton, Alberta and submitted to the journal of applied polymer science entitled " Emulsion Copolymerization in A Tubular Reactor". In this paper, emulsion copolymerization was studied in a closed loop tubular reactor and the effect of flow on final conversion, particle size distribution , and copolymer composition was investigated.
- Chapter III consists of a conference paper presented in the 15th International Symposium of Chemical Reaction Engineering (ISCRE 15) in Newport beach, California and submitted to the Journal of macromolecular science entitled "Effect of

Reactor Configuration On The Emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. In this paper the effect of adding a static mixer to the configuration of the tubular reactor was studied. The final conversion, the evolution of particle size distribution, mean particle size, copolymer composition, and instantaneous copolymer composition in two different configurations were compared.

- In chapter IV, the publication " A Comparative Study On Copolymer Composition In Emulsion Copolymerization of Vinyl Acetate and Butyl Acrylate in A Tubular Reactor" is presented. This article is submitted to the Journal of Applied Polymer Science. Changing the reactivity ratios of vinyl acetate and butyl acrylate and the effect of flow rate and monomer composition in feed on the conversion of each of consisting monomers are studied in this paper.
- Conclusions and Recommendations
- Six appendices which give more detail on: the calculation of the mass conversion, calibration of reciprocating pump and the protocol for the utilization of vinyl acetate and butyl acrylate.

CHAPTER 2 EMULSION COPOLYMERIZATION IN A TUBULAR REACTOR

Reference:

Poormahdian, S., Bataille, P., "Emulsion Copolymerization in a tubular reactor", To be published in the Journal of Applied Polymer Science (March 1999)

Keywords:

emulsion polymerization, copolymerization, vinyl acetate, butyl acrylate

2.1 Synopsis

A study was conducted on the emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. It was performed at a constant temperature of 60 °C and at different fluid velocities and feed compositions. Conversion, particle size distribution, and copolymer composition were measured, respectively, with gravimetric method, laser light scattering, and nuclear magnetic resonance. Maximum conversions were found for each of the monomer compositions, this maximum conversion varied, however, with the recipe used. The amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. In lower levels of butyl acrylate particle size distribution is wide and bimodal. High levels of butyl acrylate leads to narrow and monomodal particle size distribution. Therefore the level of butyl acrylate and the velocity of fluid flowing inside the tube have strong effects on the shape (monomodal- bimodal) and the width of particle size distributions. This effect may vary in different levels of butyl acrylate and flow rate. the results obtained from copolymer composition shows that an alternative block copolymer is made during the reaction.

2.2 Introduction

Emulsion polymerization has been well studied in batch systems and to a lesser extent in CSTRs; however, there has been very little work done with tubular reactors. This is surprising in the light of potential advantages of such a system.

In 1939, Mark[1], for the first time used a tubular reactor, and in 1946, Calcott and Starkweather[2] improved the reactor. Emulsion copolymerization of styrene and butadiene was done by Feldon[3] in laminar flow. Lanthier[4] in his patent described a continuous loop recycle reactor in which the recycle loop flow rate was much greater than the reactor feed flow rate. A plug flow reactor (PFR) was used to produce seed particles for a CSTR by Ueda[5]. Ghosh and Forsyth[6] used a tubular reactor for polystyrene and formulated a model. Rollin et al.[7] studied the influence of the Reynolds number on the rate of polymerization of polystyrene in a closed-loop reactor. Vatanatham and Forsyth[8] studied the emulsion copolymerization of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) in a tube. Rollin et al.[9], for the first time, used a helical reactor in open loop. In 1981, Lynch and Kiparissides[10] simulated the turbulent experiments of Rollin et al[7] . Lee and Forsyth[11]studied the seeded polymerization of vinyl acetate in the reactor built by Vatanatham and Forsyth[8]. Bataille et al.[12] studied the copolymerization of styrene and α-methyl styrene in an open loop reactor. Lee and Poehlein[13] used a Teflon coated tubular reactor as a seed reactor for a CSTR. Shoaf and Poehlein[14] studied the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR, and tubular reactors. Bataille and Dalpé[15] studied the polymerization of vinyl acetate in a closed loop reactor. Lee et al.[16] investigated the polymerization of styrene in a continuous recycle reactor. Paquet et al.[17,18] studied emulsion polymerization in a pulsed tubular reactor. They performed their experiments in batch, CSTR, closed loop and a pulsed open loop tubular reactor. Iabbadène and Bataille[19] studied the emulsion polymerization in a pulsed tubular reactor.

No work, however, is reported on the emulsion copolymerization of vinyl acetate-butyl acrylate in a tubular reactor. The object of this paper is to fill this gap and try to understand how and why the polymerization operating conditions will affect the polymer properties.

2.3 Reactor Geometry

Most of the studies mentioned here have been done in essentially straight tubular reactors, the curved parts (the elbows) constituting only a very small proportion of the total length. A reactor of commercial interest operated with a Reynolds number in the vicinity of 2100 would be of the order of 60 to 600 meters in length depending on the tube diameter. The benefits of good heat transfer and temperature control of emulsion polymerization are generally realized by the immersion of the reactor in a heat transfer medium of substantial thermal capacity. This is difficult and costly to achieve with a linear tubular reactor and a helical configuration, however, might be considered as a viable alternative. According to the works of Eustice[20], Dean[21], Taylor22, and Srinvasan et al[23] the curvature of the tube decreases flow perturbations and increases the value of the Reynolds number at which the laminar- turbulent transition occurs. Iabbadène[24] calculated this critical Reynolds number in the vicinity of 7500 and in this work this calculation is used as a basis to design the reactor and operation.

2.4 Experimental

2.4.1 Tubular Reactor

All experiments were done in the tubular reactor shown in Figure 2-1. This system consists of an emulsion tank, an initiator tank, a purging system, a heat exchanger, a tubular reactor, a reciprocating pump and a data acquisition system. The emulsion tank with a capacity of 3 L, was jacketed and equipped with a pitch blade (P-6) impeller, and four vertical baffles with 10 mm in width, 200 mm in length, 1 mm clearance to help better mixing. The initiator tank with a capacity of 1L is also jacketed. Each tank had openings for thermocouples, feeding, nitrogen inlet, mixer shaft and for a heat exchanger.

The thermostat bath is a cylindrical glass vessel that is used to heat the jacketed vessel to the desired temperature.

The tubular reactor is a 5 meter Teflon-lined tube with an ID 2.23 cm surrounded by a stainless steel mesh, 43 cm coiled, placed in a thermostat bath, equipped with a calibrated reciprocating pump. The reciprocating pump permits to change the velocity of the circulating fluid by changing the pump speed. Temperatures of different sites of the system are recorded by means of a data acquisition system. Each part of the system can be purged separately with nitrogen.

2.4.2 Materials

Inhibited monomers, vinyl acetate(VAc) and butyl acrylate (BuA) and the other materials were used as received. The general formulations used are given in.Table 2-1.

Table 2-1: Recipes used in experiments based on 100 parts of vinyl acetate and butyl acrylate

Material	Recipe1	Recipe2	Recipe3
Vinyl acetate(monomer)	95	85	75
Butyl acrylate(monomer)	5	15	25
Distilled water	321.8	321	324.7
Sodium Lauryl sulfate(surfactant)	1.75	1.75	1.75
Potassium Persulfate(initiator)	0.24	0.24	0.24
NOPCO(Antifoaming agent)	10 drops	10 drops	10drops

2.4.3 Procedure

Emulsifier was dissolved in 1000mL distilled water together with 10 drops of NOPCO as an antifoaming agent. The initiator was dissolved in 200mL distilled water. All parts of the system including tubes, emulsion tank, and initiator tank, were purged with nitrogen. The solution of emulsifier, and the required amounts of vinyl acetate, butyl acrylate and 1500mL of distilled water were poured inside the emulsion tank. Emulsification was performed using the mixer, and continued for 50 minutes to make sure the emulsification was complete. The emulsion was then transferred to the tube. The reciprocating pump was turned on and set at the highest speed in order to reach quickly 60 °C. this took between 15 to 25 minutes depending on the recipe. When the temperature in the tube reached 60 °C, the pump was set at the desired speed to obtain the required Reynolds number. The liquid was mixed for about 30 minutes so that it reaches a constant velocity profile. After this period, the initiator solution was injected inside the tube by means of nitrogen exerted through the initiator tank. This is considered as t=0 for the emulsion copolymerization. The copolymerization continued to proceed for up to 2 hours. During the reaction, samples were collected through the sampling valve and the reaction short-stopped with hydroquinone. Finally the pump was turned off and the produced latex was discharged through the sampling valve, then the three-way valve was opened and all the system was washed with water.

Collected samples were analyzed for conversion, particle size distribution and copolymer composition. Particle size distribution was measured by using a laser light scattering from Brookhaven Instruments Corporation, connected to a BIMODAL-203AT digital correlator, where the data could be collected. For this analysis, dust-free doubled distilled water was used. The measurements were carried out by maintaining the samples in a paraffin bath at 25 °C. the data obtained from this instrument processed to have a distribution curve based on the fraction of particles.

A Brucker WH400 spectrometer (400.13 MHz) was used to obtain the molar composition of latex by NMR spectra. Knowing the CH group resonance in vinyl acetate (5.22 ppm) and -O-CH_2 group resonance in butyl acrylate (4.13 ppm), the composition was calculated from the area under each peak[25].

Reynolds numbers of 6500, 7500, 8600, and 9700 were applied to each set of experiments. The reciprocating pump was calibrated with water at 60 °C.

2.5 Results And Discussion

2.5.1 Conversion

Iabbadène and Bataille[19] showed that in emulsion copolymerization of vinyl acetate a maximum conversion was reached in the laminar-turbulent transition flow region. The copolymerization of vinyl acetate and butyl acrylate treated in a similar way and the results for final conversion versus Reynolds number are given in Figure 2-2. The results of each of the monomer feed compositions are given in this Figure.

The results of experiments with tubular reactor compared with those in batch rectors[26]. This comparison showed that the conversion obtained in tubular reactor were sufficiently below the conversion obtained in the batch reactor.

In all cases maxima are obtained. The location and the amplitude of these maximums are functions of the feed composition and the agitation.

With 5% wt. of butyl acrylate the maximum is in the turbulent flow region with a conversion of about 96% wt. When the concentration of butyl acrylate is increased to 15 % wt. two maxima appear with, however a decrease in conversion to about 67%. Below Re=6500, conversion drops into a low level because the fluid movement is not sufficient and phase separation is occurred. Interesting enough one of the maxima occurs in the turbulent flow region suggesting two different reaction mechanisms. When the level of butyl acrylate is increased to 25% wt. we have a further flattening of the conversion curve but again two peaks appear one in the laminar flow region and the other one in the turbulent flow region.

By increasing the amount of butyl acrylate in the feed one can notice a shift of the maximum conversions towards the turbulent flow region. The butyl acrylate has a negative effect on the final conversion in some regions and positive effect in some other regions.

In Figure 2-3 and Figure 2-4 are plotted the number of particles in one drop of laser light scattering sample (0.05 ml) as a function of time at laminar-turbulent transition flow region and turbulent flow , and at 3 levels of monomer feed compositions. For the laminar-turbulent transition flow system (Figure 2-3) the number of particles produced is the highest when the feed composition is at 5% wt butyl acrylate and 95% wt vinyl acetate. As the butyl acrylate is increased to 15% wt then to 25% wt there is a general drop in the number of particles formed. This type of ordering is similar to the one for the final conversion given in Figure 2-2. For the turbulent flow as shown in Figure 2-4 , the highest level of particles is obtained initially with 15% wt butyl acrylate and 85% wt vinyl acetate. After 20 minutes, however, the order of importance of the number of particles formed reverts back to the one formed for the laminar-turbulent transition flow. It could be said that in tubular reactor the amount of butyl acrylate in system has a direct effect on the number of produced particles and on final conversion.

2.5.2 Particle Size

2.5.2.1 Particle Size Distribution

The evolution of particle size distribution was monitored continuously during the reaction. Secondary nucleation was observed as a bimodal particle distribution appeared, in the early stages of the polymerization. This is shown in 2-5 for the system of 5% wt butyl acrylate and 95% wt vinyl acetate in the feed at a highly turbulent flow (Re=9700). The existence of secondary nucleation confirms that there is homogeneous nucleation during the emulsion copolymerization due to the water solubility of vinyl acetate[27].

All the particle size distributions related to high conversion conditions in different compositions of feed were compared in Figure 2-6. In this Figure it can be seen that the final latex in reaction with 95 wt% vinyl acetate and 5 wt% butyl acrylate has a broad and bimodal particle size distribution. However the final latex of 85 wt% vinyl acetate, 15 wt% butyl acrylate, and 75 wt% vinyl acetate, 25 wt% butyl acrylate have both narrow and monomodal particle size distribution. In reaction with 85 wt% vinyl acetate it is seen that there is always in two different flow regions where a monomodal particle size distribution is obtained, but the particle size distribution obtained in highly-turbulent flow is narrower than particle size distribution obtained in laminar-turbulent transition flow.

In case of 75 wt% vinyl acetate, also, both particle size distributions are monomodal but the one obtained in laminar flow is narrower than the one obtained in turbulent flow.

In general it could be said that in emulsion copolymerization of vinyl acetate and butyl acrylate in tubular reactor in contrast to the batch reactors [26] and like semi-continuous reactors[26] by increasing the quantity of butyl acrylate in feed a narrow particle size distribution is obtained. It was found that the amount of butyl acrylate and the velocity of fluid have strong effects on the shape (monomodal - bimodal) and on the distribution of the particle size. This effect may change with different butyl acrylate contents and fluid velocities. So, it could be said that in addition to the chemical composition of the feed flow rate has also a dominant effect on the properties of final latex including particle size distribution and mean particle size.

2.5.2.2 Mean Particle Size

The evolution of mean particle size for the experiments with high conversions is shown in Figure 2-7.

In all three cases, mean particle size decreases during the reaction and reaches a nearly constant value. Clearly, the amount of butyl acrylate in the feed and also the fluid velocity have a strong effect on the mean particle size. In all 3 plots it can be seen that ,like semi-continuous[27] and in contrast to batch reactor[28] , by increasing the butyl acrylate in feed, final mean particle size tends towards smaller diameters

It is proposed that in all cases during the course of reaction secondary nucleation cause to have old and new particles. As the reaction proceeds the distribution of the new particles shifts gradually such that their average diameter tends towards the mean particle size of old particles. These results suggest the formation of new particles during the polymerization process. The proposed explanation is that, as the conversion in a particle milieu becomes unfavorable to the surfactant and the emulsifier thus released permits the creation of new micelles, and consequently, of new particles.

2.5.3 Copolymer Composition

The composition of the copolymer was monitored throughout the polymerization by N.M.R . Results for the system of 15% butyl acrylate and 85% vinyl acetate at turbulent flow are given in Figure 2-8. In regard with the reactivity ratios of vinyl acetate (r_1=0.024) and butyl acrylate (r_2=10.67)[25] it suggest that the polymer would be constituted of two long chains of vinyl acetate, and butyl acrylate attached together. i.e. a block copolymer. Figure 2-8 shows sometimes that the vinyl acetate contents of copolymer increases and then decreases. This suggests that during the reaction, an alternating block copolymer is made. To confirm this idea the instantaneous copolymer composition was calculated from the NMR data. Instantaneous copolymer composition being defined as the ratio of vinyl acetate (electron donor) moles to the butyl acrylate (electron acceptor) moles in copolymer[29]. If instantaneous copolymer composition is between 1 and 2 the latex is an alternating copolymer, and if it exceeds to more than 2 the latex is an alternating block copolymer. Figure 2-9 confirms this idea. It is seen that during the progress of reaction instantaneous copolymer composition increases with fluctuations. It is proposed that the tendency of monomers in order to react changes during the reaction and blocks of vinyl acetate and butyl acrylate is made. Finally we can obtain a latex with an alternating block structure. In other words in a tubular reactor it is possible to decrease the composition drift and avoid the large composition drift existing with copolymerization in a batch reactor [27].

2.6 Conclusion

Emulsion copolymerization of vinyl acetate and butyl acrylate was done in a tubular reactor in constant temperature of 60 °C and different fluid velocities and feed compositions. It was found that depending on the monomers composition in feed there is (are) region(s). that conversion is maximum. These regions are not the same in different recipes. Also it was found that the amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. Studies on particle size distribution showed that recipes with lower quantities of butyl acrylate have a wide and bimodal particle size distribution for final latex, and recipes with higher butyl acrylate contents have a narrow and monomodal particle size distribution. So the amount of butyl acrylate and the velocity of fluid flowing inside the tube have strong effects on the shape (monomodal- bimodal) and the width of particle size distributions. This effect may vary in different butyl acrylate contents and fluid velocities. In investigating copolymer composition it was found that an alternative block copolymer is made during the reaction.

2.7 Acknowledgment

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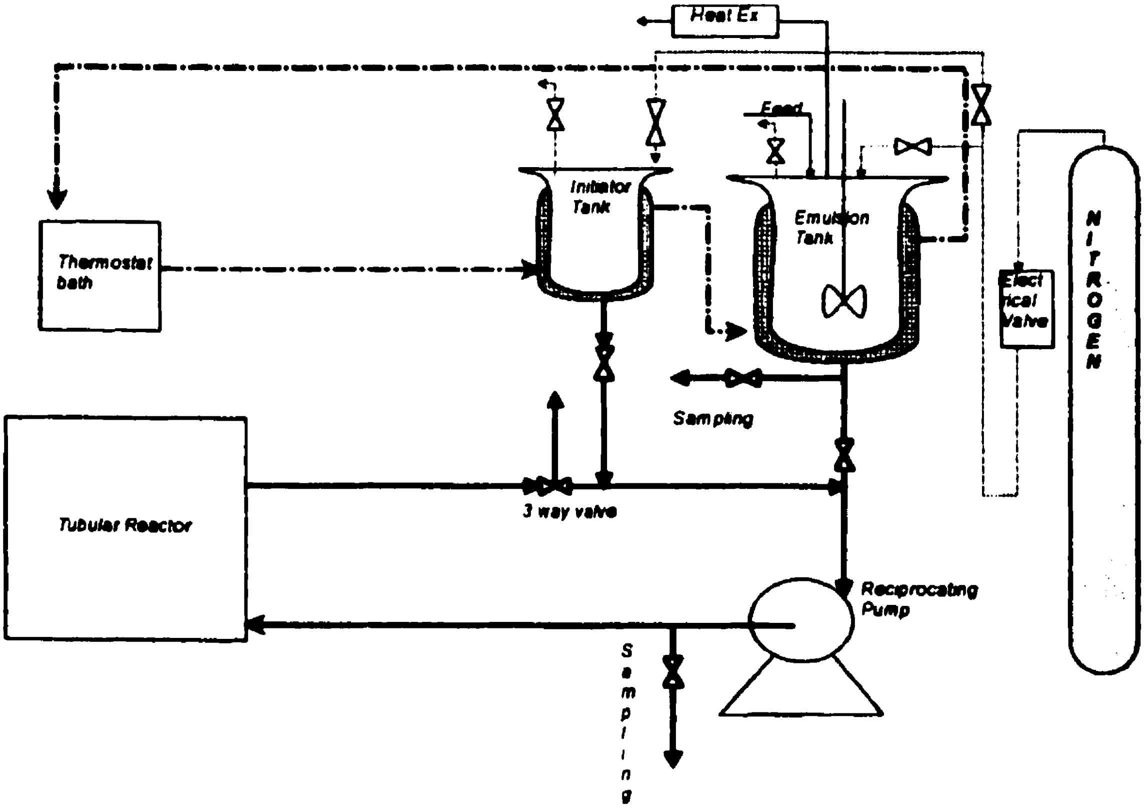

Figure 2-1: Reactor Design

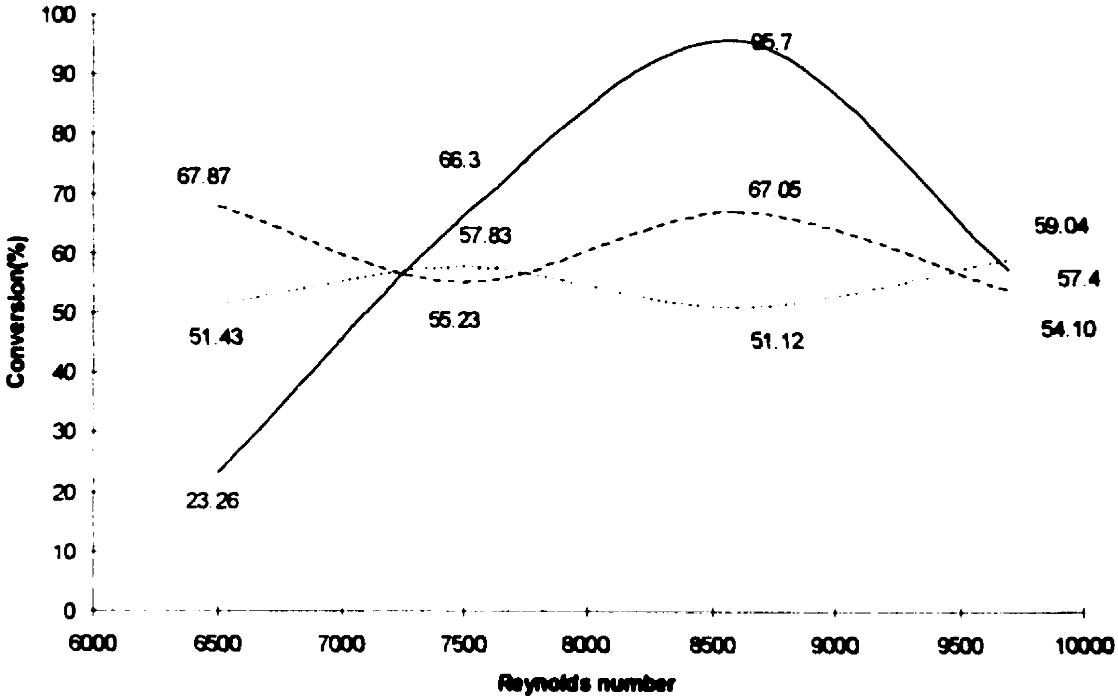

Figure 2-2: Total conversion as a function of Reynolds number in the emulsion copolymerization of vinyl acetate and butyl acrylate . Vinyl acetate -Butyl acrylate ratios: (——) 95/5, (——) 85/15, (——) 75/25

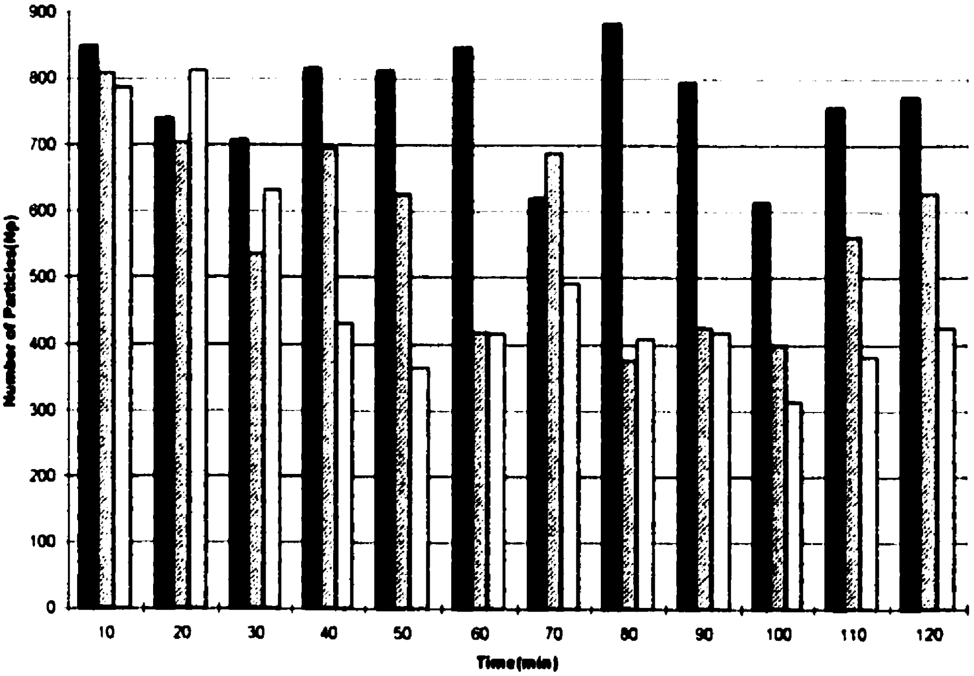

Figure 2-3: Number of particles in different times of reaction [Re=7500, laminar-turbulent transition flow]

Vinyl acetate -Butyl acrylate ratios: (■) 95/5, (▨) 85/15, (□) 75/25

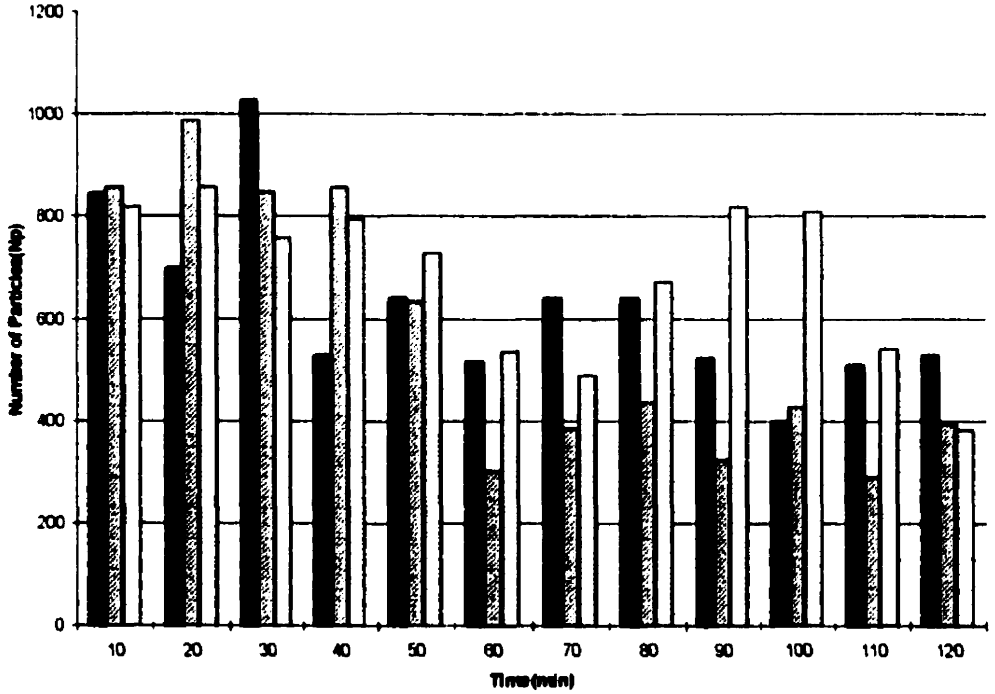

Figure 2-4: Number of particles in different times of reaction [Re=9700,highly-turbulent flow]

Vinyl acetate -Butyl acrylate ratios: (■) 95/5, (▨) 85/15, ☐) 75/25

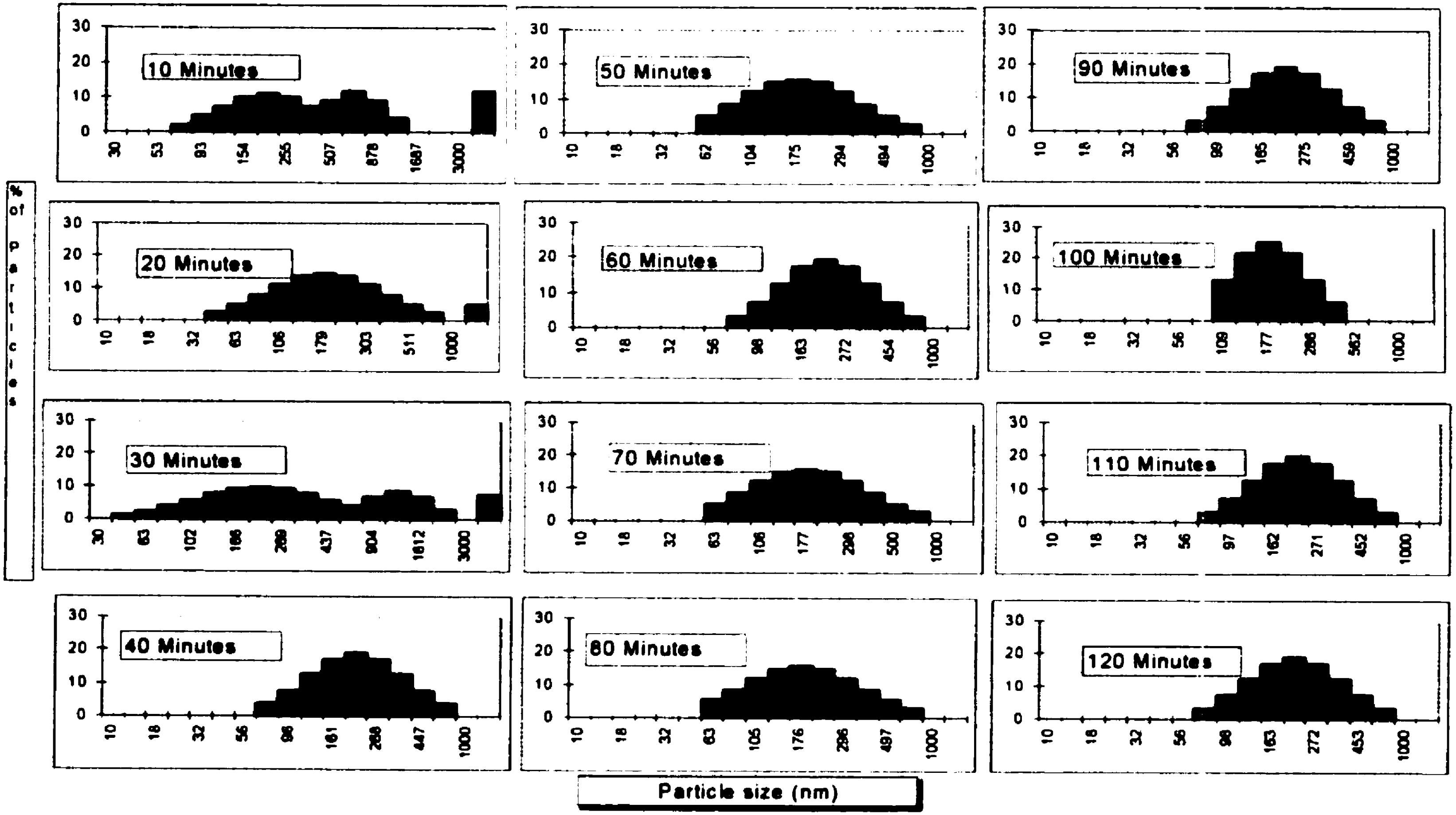

Figure 2-5 The evolution of particle size distribution in emulsion copolymerization of 95wt% vinyl acetate and 5 wt% butyl acrylate in highly-turbulent flow (Re=9700)

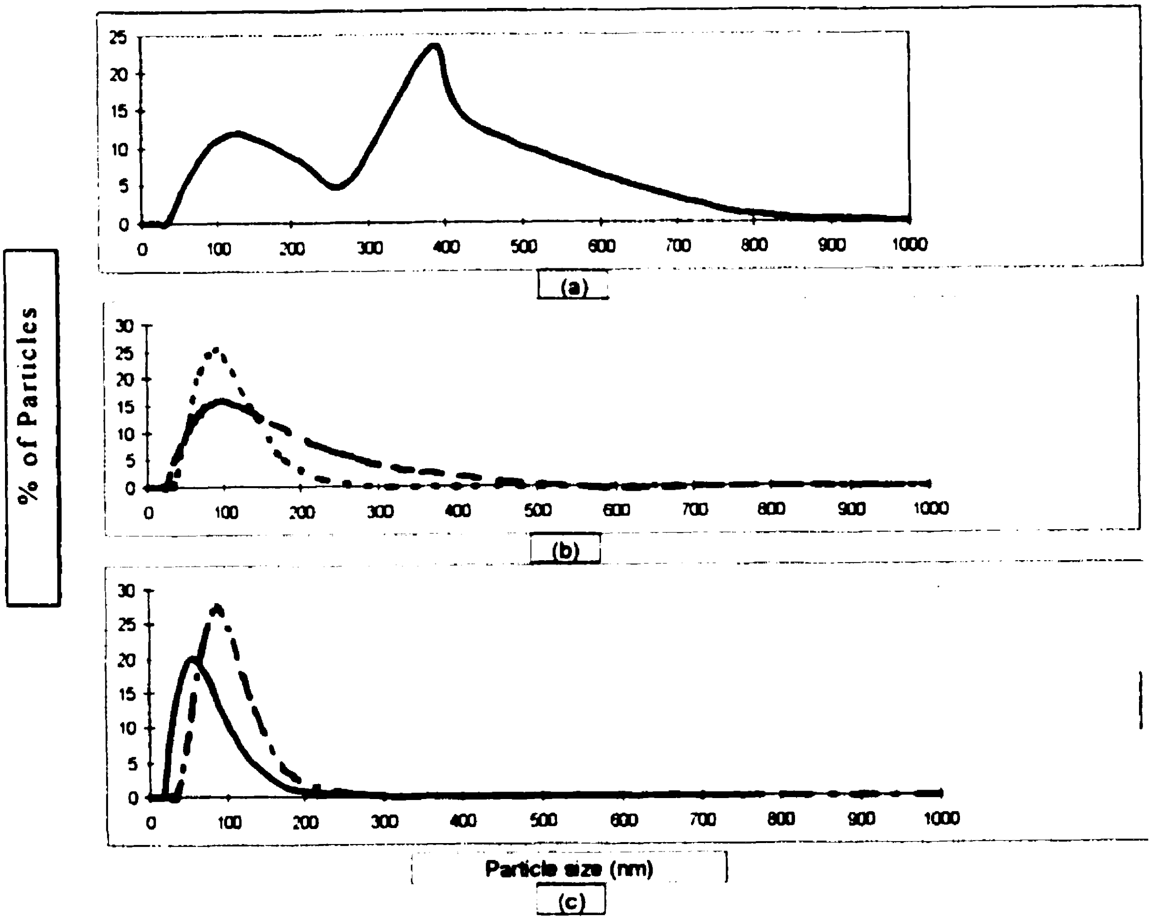

Figure 2-6: Final particle size distributions related to the cases with maximum conversion

(a) 5 wt% butyl acrylate , (————) Re = 8600

(b) 15 wt% butyl acrylate , (— — —) Re = 7500, (................) Re = 9700

(c) 25 wt% butyl acrylate, (– · – · –) Re = 6500, (————) Re = 8600

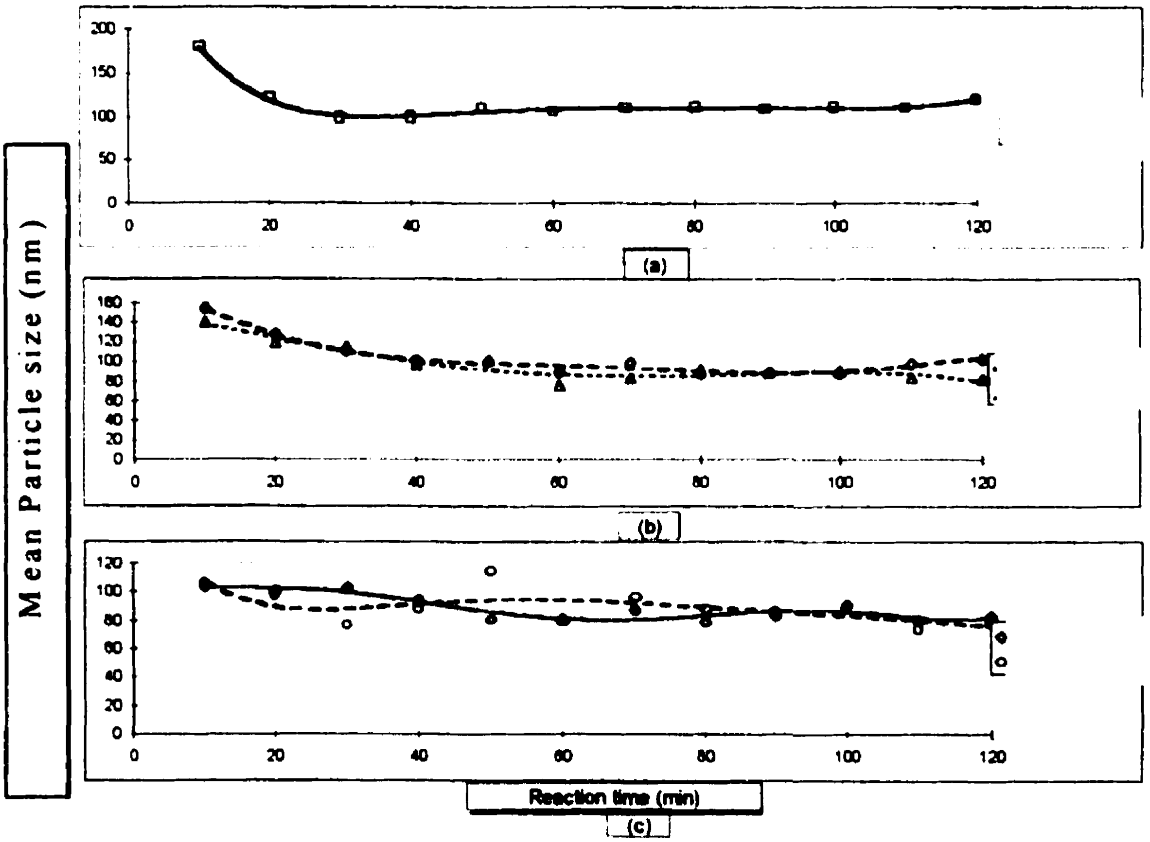

Figure 2-7: The evolution of mean particle size related to the cases with maximum conversion

(a) 5 wt% butyl acrylate, (□) Re=8600

(b) 15 wt% butyl acrylate, (◇) Re=7500, (△) Re=9700

(c) 25 wt% butyl acrylate, (◇) Re=6500, (○) Re=8600

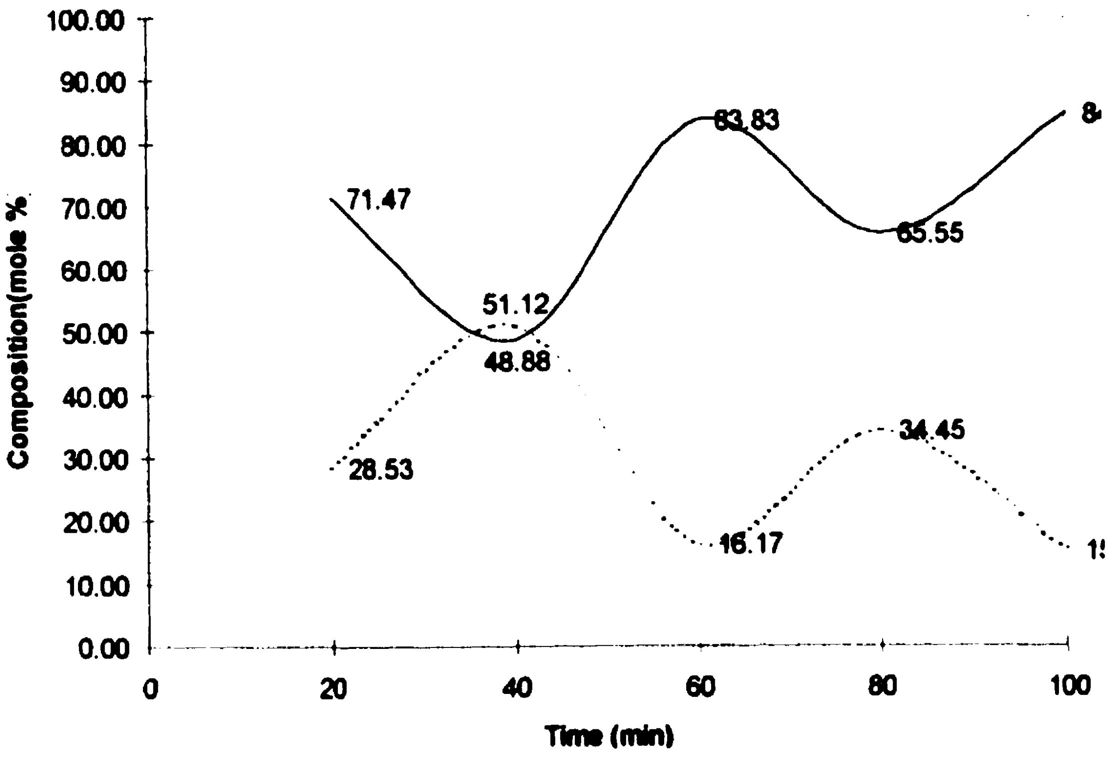

Figure 2-8: Copolymer composition of poly vinyl acetate-butyl acrylate latex made from feed containing 85 wt% vinyl acetate and 15 wt% butyl acrylate , in turbulent flow (Re=8600)
(————) % of Vinyl acetate, (··············) % of Butyl acrylate.

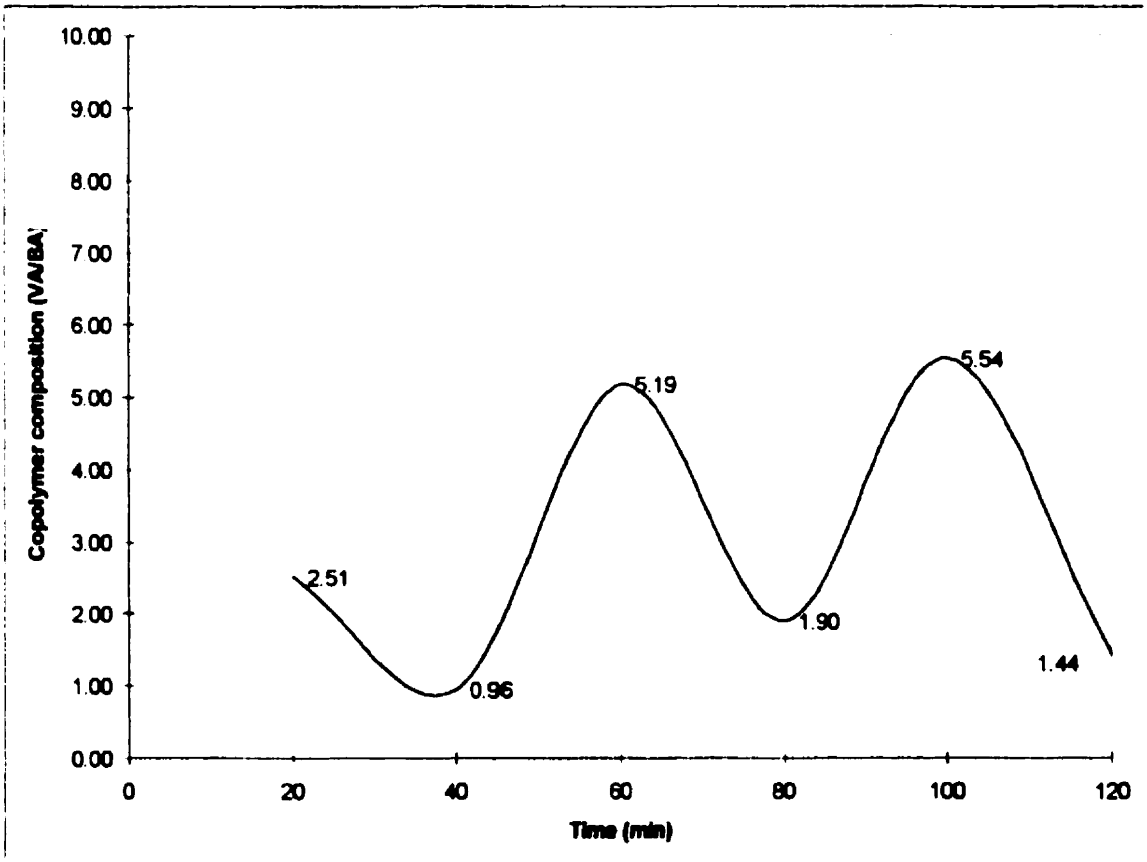

Figure 2-9: The evolution of instantaneous copolymer Composition during emulsion copolymerization (85 wt% vinyl acetate and 15 wt% butyl acrylate, turbulent flow (Re=8600)

CHAPTER 3 : EFFECT OF REACTOR CONFIGURATION ON THE EMULSION COPOLYMERIZATION OF VINYL ACETATE-BUTYL ACRYLATE IN A TUBULAR REACTOR

Reference:

Poormahdian, S., Bataille, P., "Effect Of Reactor Configuration On The emulsion Copolymerization Of Vinyl Acetate-Butyl Acrylate In A Tubular Reactor", Submitted to Journal of Macromolecular science (March 1999)

Keywords : emulsion polymerization, copolymerization, vinyl acetate, butyl acrylate

3.1 Context [1]

In chapter 2 , emulsion copolymerization of vinyl acetate and butyl acrylate was tested in a tubular reactor- the aim was to evaluate the behavior of copolymerization in the tubular reactor. It has been shown that there are regions that in which conversion of polymerization is maximum. The flow rate (designated as Reynolds number), quantity of vinyl acetate and butyl acrylate in feed have strong effect on the particle size distribution , copolymer composition and the final structure of produced copolymer. Also the configuration of the reactor, and the existence of static mixer has another effect on the above mentioned characteristics, which is the subject of this chapter. The experimental results shows the existence of static mixer has a destructive effect on the final conversion of polymerization, but can help to obtain an alternating block copolymer with short blocks which is similar to an alternating copolymer.

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[1] This section is not included in the original manuscript. It only serves as a transition between papers of thesis

3.2 Abstract

A study was conducted on the emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. The effect of a static mixer was studied on the final conversion, particle size distribution, copolymer composition, and instantaneous copolymer composition. It was found that there is a flow region in which the emulsion copolymerization has maximum conversion. This region could be displaced by changing feed composition, and by the presence of a static mixer. A static mixer can change the distribution of particle sizes in final latex, and has strong effect on the molecular structure of the product.

3.3 Introduction

Emulsion polymerization has been well studied in batch systems and to a lesser extent in CSTRs; however, there has been very little work done with tubular reactors. This is surprising in the light of potential advantages of such a system.

In 1939, Mark [1], used a tubular reactor for the first time, and in 1946 Calcott and Starkweather improved the reactor [2]. Emulsion copolymerization of styrene and butadiene was done by Feldon [3] in laminar flow. Lanthier [4] in his patent described a continuous loop recycle reactor in which the recycle loop flow rate was much greater than the reactor feed flow rate. In 1971 a plug flow reactor (PFR) was used to produce seed particles for a CSTR by Ueda [5]. In 1976 , Ghosh and Forsyth [6] used a tubular reactor for polystyrene and formulated a model. Rollin et al.[7] studied the influence of the Reynolds number on the rate of polymerization of polystyrene in a closed-loop reactor.

They found a limiting conversion below the final conversion obtained in a comparative batch reactor. In all of these reactors previously discussed one of the major problems was plugging in the reactors. Vatanatham and Forsyth [8] studied the emulsion copolymerization of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) in a tube. Particle size data for the tubular reactor suggested that the particle size distribution is only slightly broader in a tubular reactor than in a batch system. Rollin et al. [9], for the first time, used a helical reactor in open loop. The results obtained in the open loop reactor were similar to the closed loop experimental results- they found a maximum rate of polymerization at the laminar-turbulent transition flow. Also one of the major problems for a tubular reactor, plugging was solved. In 1981, Lynch and Kiparissides [10] simulated the turbulent experiments of Rollin et al [7]. Their monodisperse model included axial dispersion if initiator, micelle nucleation, and particle loss by coalescence. Lee and Forsyth [11] studied the seeded polymerization of vinyl acetate in the reactor built by Vatanatham and Forsyth [8]. Bataille et al. [12] studied the copolymerization of styrene and α-methyl styrene in an open loop reactor. The use of a seed latex in the presence of secondary nucleation produced bimodal particle size distribution. They also reported stable oscillations in conversion when the exit conversion was more than 30%. Lee and Poehlein [13] used a Teflon coated tubular reactor as a seed reactor for a CSTR. By introducing nitrogen plugs to control the residence time, the reactor operated as a plug flow reactor. Limiting the conversion to less than 10% to ensure that no nucleation occurred in the subsequent CSTR, they found the tubular reactor to operate identically to a batch reactor. Shoaf and Poehlein [14] studied the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR, and tubular reactors. They report phase separation and plugging for some of the experiments at the low flow rates. To eliminate the plugging, they increased the flow rate and added a larger diameter tube to the end of the smaller tube. Bataille and Dalpé [15] studied the polymerization of vinyl acetate in a closed loop reactor. They reported limiting conversions (50 to 60%) occurred for all cases. Also they found an optimum recirculation rate.. Lee et al. [16] investigated the polymerization of styrene in a continuous recycle reactor. They found with recirculation rates much larger than the reactor feed rate, the reactor operated similar to a CSTR. Paquet et al. [17,18] studied emulsion polymerization in a pulsed tubular reactor. They performed their experiments in batch, CSTR, closed loop and a pulsed open loop tubular reactor. The results of experiments showed that in the open loop reactor plugging was occurred and after adding a pulsation source plugging was eliminated. At low residence times, monomer conversion in a CSTR was low and oscillatory. Conversion was much higher in batch and tube reactors. At high residence times, the conversion was the same for all three reactors. Iabbadène and Bataille [19] studied the emulsion polymerization in a pulsed tubular reactor. In this work it was found that agitation or flow was important on vinyl acetate emulsion polymerization in a tubular loop reactor. The optimum conversion was occurred in a narrow zone. Preselection of particle size was possible by variation of flow rate and reaction time. Emulsifier concentration had an effect on conversion and particle size.

The only work reported on emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor is by Poormahdian and Bataille [20]. The first in these series where no static mixer was used. In this paper the effect of a static mixer was studied and results are compared with the ones obtained without a static mixer.

3.4 Reactor Geometry

Most of the studies mentioned here have been done in essentially straight tubular reactors, the curved parts (the elbows) constituting only a very small proportion of the total length. A reactor of commercial interest operated with a Reynolds number in the vicinity of 2100 would be of the order of 60 to 600 meters in length depending on the tube diameter. The benefits of good heat transfer and temperature control of emulsion polymerization are generally realized by the immersion of the reactor in a heat transfer medium of substantial thermal capacity. This is difficult and costly to achieve with a linear tubular reactor and a helical configuration, however, might be considered as a viable alternative. According to the works of Eustice [21], Dean [22,23], Taylor [24], and Srinvasan et al [25] the curvature of the tube decreases flow perturbations and increases the value of the Reynolds number at which the laminar- turbulent transition occurs. Iabbadène [26] calculated this critical Reynolds number in the vicinity of 7500 and in this work this calculation is used as a basis to design the reactor and operation.

3.5 Experimental

3.5.1 Tubular Reactor

All experiments were done in the tubular reactor shown in Figure 3-1. This system consists of an emulsion tank, an initiator tank, a purging system, a heat exchanger, a tubular reactor equipped with a static mixer, a reciprocating pump and a data acquisition system. The emulsion tank with a capacity of 3 L, was jacketed and equipped with a pitch blade (P-6) impeller ,and four vertical baffles with 10 mm in width, 200 mm in length, 1 mm clearance to help better mixing. The initiator tank with a capacity of 1L is also jacketed. Each tank had openings for thermocouples, feeding, nitrogen inlet, mixer shaft and for a heat exchanger.

The thermostat bath is a cylindrical glass vessel that is used to heat the jacketed vessel to the desired temperature.

The tubular reactor is a 5 meter Teflon-lined tube, 2.23 cm ID surrounded by a stainless steel mesh, 43 cm coiled, placed in a thermostat bath, equipped with a calibrated reciprocating pump. The reciprocating pump permits to change the velocity of the circulating fluid by changing the pump speed. Temperatures of different sites of the system are recorded by means of a data acquisition system. Each part of the system can be purged separately with nitrogen.

3.5.2 Materials

Inhibited monomers, vinyl acetate(VAc) and butyl acrylate (BuA) (Hydroquinone in Vac and Monomethyl ether in BuA) and the other materials were used as received. The general formulations used are given in Table 3-1.

Table 3-1: Recipes used in experiments based on 100 parts of vinyl acetate and butyl acrylate

Material	Recipe 1	Recipe 2	Recipe 3
Vinyl acetate(monomer)	95	85	75
Butyl acrylate(monomer)	5	15	25
Distilled water	321.8	321	324.7
Sodium Lauryl sulfate(surfactant)	1.75	1.75	1.75
Potassium Persulfate(initiator)	0.24	0.24	0.24
NOPCO(Antifoaming agent)	10 drops	10 drops	10 drops

3.5.3 Procedure

Required amounts of initiator, emulsifier, monomers and distilled water are weighted and prepared. Emulsifier was dissolved in 1000mL distilled water together with 10 drops of NOPCO as an antifoaming agent. The initiator was dissolved in 200mL distilled water. All parts of the system including tubes, emulsion tank, initiator tank, were purged with nitrogen. The solution of emulsifier, and the required amounts of vinyl acetate, butyl acrylate and 1500mL of distilled water were poured inside the emulsion tank. Emulsification was performed using the mixer, and continued for 50 minutes to make sure the emulsification is complete. The emulsion was then transferred to the tube. The reciprocating pump was turned on and set at the highest speed in order to reach quickly 60 °C. This took between 15 to 25 minutes depending on the recipe. When the temperature in the tube reached 60 °C, the pump was set at the desired speed to obtain the required Reynolds number. The liquid was mixed for about 30 minutes so that it reaches a constant velocity profile. After this period, the warmed up initiator solution was injected inside the tube by means of nitrogen exerted through the initiator tank. This is considered as t=0 for the emulsion copolymerization. The copolymerization continued to proceed for up to 2 hours. During the reaction, samples were collected through the sampling valve and the reaction short-stopped with hydroquinone. Finally the pump was turned off and the produced latex was discharged through the sampling valve, then the three-way valve was opened and all the system was washed with water.

Collected samples were analyzed for conversion, particle size distribution and copolymer composition. Particle size distribution was measured by using a laser light scattering from Brookhaven Instruments Corporation, connected to a BIMODAL-203AT digital correlator, where the data could be collected. For this analysis, dust-free doubled distilled water was used. The measurements were carried out by maintaining the samples in a paraffin bath at 25 °C . The data obtained from this instrument processed to have a distribution curve based on the fraction of particles.

A Brucker WH400 spectrometer (400.13 MHz) was used to obtain the molar composition of latex by NMR spectra. Knowing the CH group resonance in vinyl acetate (5.22 ppm) and -O-CH_2 group resonance in butyl acrylate (4.13 ppm), the composition was calculated from the area under each peak [27].

Reynolds numbers of 6500, 7500, 8600, and 9700 were applied to each set of experiments. The reciprocating pump was calibrated with water at 60 °C. Because the viscosity of water and emulsion are very close at 60 °C, the results of the calibration with water could be applied for the emulsion. To calculate the Reynolds number, all the physical properties of the emulsion were considered at 60 °C (reaction temperature).

Two groups of experiments were done. In the first group, the experiments described above were done without the static mixer, and in the second group the experiments of the first group were done in the presence of a static mixer. In this case a Teflon coated static mixer is placed at the outlet of reciprocating pump.

3.6 Results And Discussion

3.6.1 Conversion

In both groups of experiments, the maximum conversion in each experiment as a function of the Reynolds number is shown in Figure 3- 2. Figure 3- 2-a shows the effect of flow in the absence of a static mixer. It can be seen that reaction with 5wt % butyl acrylate and 95wt % vinyl acetate reaches its maximum in the early of turbulent flow (Re=8600). In Reynolds numbers less than 8600, due to strong possibility of phase separation and coagulation of particles, the reaction conversion is limited to small values. In Reynolds numbers greater than 8600, coagulation is the main cause of low conversions. These results are in agreement with the results of Lynch and Kiparissides [10]. Reactions containing 15wt % butyl acrylate and 85wt% vinyl acetate have a sinusoidal behavior. In laminar flow (Re=6500) conversion is 51.4 wt%. The Conversion in laminar-turbulent transition flow (Re=7500) is increased to 57.8 wt % . In the early of turbulent flow, once again, it is decreased to 51.1wt %, and finally, in highly turbulent flow (Re=9700) it is increased to 59.0wt %.In general, it can be said that coagulation has a strong effect on all emulsion copolymerizations in a tubular reactor and limits the conversion up to 59.0wt %. This effect is amplified in some regions.

Emulsion copolymerizations containing 25wt % butyl acrylate and 75wt % vinyl acetate have, also, a sinusoidal behavior that is exactly in contrast with the previous case. The effect of coagulation is more dominant and the final conversion is limited to 67.9wt % polymer in laminar flow.

In all cases, coagulation causes a reduction in the number of polymer particles, and finally a reduction in the rate of emulsion copolymerization. It should be noted that in the laminar flow region, also phase separation in the case of 5 wt % butyl acrylate an 95 wt % vinyl acetate , helps to limit the efficiency of emulsion copolymerization.

Figure 3- 2-b shows the effect of a static mixer. It can be seen that except for the case of 95 wt % vinyl acetate and 5wt % butyl acrylate in the feed, the behavior in all cases is similar. The curve related to 85 wt % vinyl acetate in the feed shows that with an increase in the Reynolds number (or fluid velocity) the final conversion improves and in highly turbulent flow (Re=9700) reaches its maximum (79.4wt %). The conversion related to the feed containing 15 wt % butyl acrylate has a sinusoidal behavior. In the laminar flow region conversion reaches 42.4wt % . In the laminar- turbulent transition flow region it increases to 67.3 wt % , and then in the turbulent flow region it decreases to 51.8wt %. By increasing the Reynolds number in the highly turbulent flow region conversion reaches 62.2 wt %. In this case the maximum conversion is limited to 67.3 wt % in the laminar-turbulent transition flow region. In the case of 75 wt % vinyl acetate, a sinusoidal behavior is also seen. In the laminar flow region the conversion is 43.1 wt %, which increases in

the laminar-turbulent flow region to 58.7 wt %, and then decreases to 51.7wt % in the turbulent flow region. Finally it increases once more and reaches 65.16 in the highly turbulent flow, which is the maximum conversion obtained.

In general the presence of the static mixer, which applies a high shear on the particles will destroy them. Also coagulation will have a major effect on the maximum conversion of all the experiments. This shear and coagulation will decrease the final conversion. In all cases coagulation causes a decrease in the number of polymer particles and prevents the reaction progress. It should be noted that in the laminar flow region in the case of a feed containing 5 wt % butyl acrylate, phase separation limits the reaction progress and the conversion.

3.6.2 Particle Size Analysis

This analysis is restricted to the experiments with maximum conversion. First the evolution of particle size during the reaction is analyzed then this analysis is extended to the mean particle size of the latex.

3.6.2.1 Particle Size Distribution

In Figure 3-3 the evolution of particle size distribution during the emulsion copolymerization is shown when the content of butyl acrylate in the feed is 5 wt % . Figure 3- 3-a shows the particle size distribution in absence of a static mixer the maximum conversion of 95.7 wt%.This reaction is done in turbulent flow region (Re=8600), initially a trimodal with wide distribution is produced. The distribution becomes narrow and changes to monomodal after 30 minutes. The general form of this distribution does not change during the rest of the reaction. At the end of the emulsion copolymerization a secondary nucleation causes a change of the distribution which is changed to a bimodal one. Generally in this region of flow the number of nuclei generated at the early of reaction is very high and prevents secondary nucleation during the reaction. The final latex has the particle sizes in the range of 45 to 438 (nm).

Figure 3-(3-b) shows the particle size distribution variation during the emulsion copolymerization previously described with, however, the presence of a static mixer. This reaction is done in highly turbulent flow region (Re=9700) and reaches a maximum conversion of 79.4 wt %. It can be seen that after 10 minutes the particle size distribution is monomodal and after 20 minutes and 50 minutes the curve change to a bimodal and then monomodal again. During the reaction there is essentially no change in the particle sizes and its distribution and it is only at the end of reaction that the final PSD curve becomes bimodal and wider. This suggests that at the early part of the reaction, the maximum number of active particles are formed and a secondary nucleation decreased to its minimum level. That is why that the PSD curves remain monomodal until nearly the end of the reaction. Due to the existence of static mixer , a high shear rate is applied to the particles which destroy them, and flocculation occurs. Flocculation causes an increase in the particle sizes and change the distribution to a bimodal one. The final latex is consisted of particles in the range of 74 to 1000 (nm).

In Figure 3-4 the evolution of particle size distribution during the emulsion copolymerization is shown when the content of butyl acrylate in the feed is 15 wt % . Figure 3- 4-a shows the particle size distribution for the emulsion copolymerization which reached a 59.04 wt % conversion in the absence of the static mixer. This reaction is done in a highly turbulent flow (Re=9700). It can be seen that the emulsion copolymerization starts with a bimodal particle size distribution and remains for 50 minutes after which the distribution changes to monomodal are one up to the end of the reaction. With a narrow particle size distribution of 50 to 230 nm, nucleation is nearly completed in the early part of the reaction. There is no secondary nucleation observed during the second half of the reaction.

Figure 3-4-b shows the particle size distribution variation for the emulsion copolymerization previously described with however the presence of a static mixer. This reaction is done in laminar-turbulent transition flow region (Re=7500) and reaches a maximum conversion of 67.3 wt %. The emulsion copolymerization starts with a bimodal particle size distribution. During the evolution of emulsion copolymerization it changes to monomodal system and remains as such up to the end of the reaction. There is a small shift toward smaller particles during the reaction from the up to 80 minutes after which the particle size distribution becomes narrower and monomodal, and then it becomes wider. The final particle size distribution is monomodal and wide (38-306 nm). It seems due to the increase of the amount of butyl acrylate in the emulsion, the fluctuation decreases and the secondary nucleation is at a minimum .

The results of 25%wt is similar to those obtained with 15%wt butyl acrylate in feed.

3.6.2.2 Mean particle size

3.6.6.2.1 Effect Of Flow Rate

In studying the effect of flow rate on mean particle size evolution it is observed that in absence of static mixer ,when instability occurs the particle size distribution is high and fluctuates during its evolution. In regions where the conversion is maximum the mean particle size reaches quickly a plateau and it remains there to the end of the reaction. Generally it is observed that mean particle size is reduced with time and reach to a constant level. as shown in Figure 3- 5-a.

In the case where a static mixer is present, there is no big fluctuations in mean particle size during the reaction. Generally mean particle size decreases with an increase in fluid velocity, as shown in Figure 3- 5-b.

3.6.6.2.2 Effect Of Monomers Composition In Feed

In absence of static mixer it is observed that in all flow regions, an increase in the butyl acrylate content in feed causes to decrease mean particle size and the mean particle size reaches sooner a plateau . Figure 3- 6-a shows the feed containing 25 wt % butyl acrylate has the smallest mean particle size , and then 15 wt % and 5 wt % stand in second and third place.

At the presence of static mixer is also observed that an increase in the amount of butyl acrylate in feed causes a decrease in mean particle size. This can be seen in each increment of time during the reaction. as in previous case the lesser the change between monomodal and bimodal evolution of particle size distribution helps to minimize the fluctuation during mean particle size evolution. This can be seen in Figure 3- 6-b.

3.7 Copolymer Composition

In this section instantaneous copolymer composition, mole fraction of vinyl acetate and butyl acrylate in copolymer are calculated from data obtained from NMR spectroscopy.

3.7.1 Mole Fraction Of Vinyl Acetate In Copolymer

Mole fraction of vinyl acetate added to the vinyl acetate-butyl acrylate copolymer is shown as F_1 and defined by the following equation [27]:

$$F_1 = \frac{(r_1.f_1^2 + f_1.f_2)}{(r_1.f_1^2 + r_2.f_2^2 + 2f_1.f_2)} \qquad (3\text{-}1)$$

in this equation r_1 ,r_2, f_1, and f_2 are, respectively, reactivity ratio of vinyl acetate and butyl acrylate, mole fraction of vinyl acetate and butyl acrylate in feed. The reactivity ratios used in this work, where as determined by other workers [28] are : r_1= 0.024, and r_2= 10.67. Variation of F_1 as a function of Reynolds number is shown in Table 3-2 for both types of reactions done in absence and in presence of static mixer. In Table 3-2-a it can be seen, that in absence of static mixer, with 95 wt % vinyl acetate in feed, an increase in Reynolds number causes to increase in F_1, but after going to Reynolds number of 8600 F_1 decreases slightly. With 85 wt % vinyl acetate in feed, F_1 has a nearly sinusoidal behavior. From laminar to laminar-turbulent transition flow regime, F_1 increases and after passing the transition flow region it decreases. In highly turbulent flow F_1 increases, once more , and reaches its highest level of 0.83. With 75 wt % vinyl acetate in feed, final F_1 decreases as we go from laminar to transition flow region. By increasing the Reynolds number F_1 increases linearly. In general it can be said that with decrease in vinyl acetate in the feed content, there is a decrease as expected in vinyl acetate in the copolymer, however this does not occur in laminar flow region.

In Table 3-2-b ,in the presence of static mixer, with 95 wt % vinyl acetate in feed, F_1 increases with increasing Reynolds number. In laminar-turbulent transition flow region it reaches a plateau. In turbulent flow region F_1 increases once more. With 85 wt % vinyl acetate in feed, F_1 increases with Reynolds number from laminar to transition flow. After that it decreases with increasing Reynolds number. With 75 wt % vinyl acetate in feed, F_1 shows a sinusoidal behavior. It increases from laminar to transition flow, then decreases to turbulent flow, and by increasing Reynolds to highly turbulent flow it increases again. It can be said each case has a unique behavior , and generally by decreasing the content of vinyl acetate in feed , its mole fraction also decreases in copolymer, as to be expected.

Table 3-2: Mole fraction of vinyl acetate in copolymer as a function of Reynolds number in emulsion copolymerization of vinyl acetate-butyl acrylate (a) without static mixer (b) using static mixer.

(a)

	F_1 in different vinyl acetate-butyl acrylate ratios		
Re	95/5	85/15	75/25
6500	0.62	0.73	0.71
7500	0.95	0.75	0.63
8600	0.97	0.71	0.68
9700	0.93	0.83	0.73

(b)

	F_1 in different vinyl acetate-butyl acrylate ratios		
Re	95/5	85/15	75/25
6500	0.79	0.69	0.50
7500	0.93	0.81	0.64
8600	0.92	0.80	0.56
9700	0.95	0.77	0.67

3.7.2 Instantaneous Copolymer Composition

Instantaneous copolymer composition (m) is defined as the ratio of vinyl acetate (electron donor) moles to butyl acrylate (electron acceptor) moles in copolymer made at a certain time during the emulsion copolymerization [28]. It should be noted that there are two kinds of copolymers: first the copolymers containing equal amounts of electron donor and electron acceptor (m=1). In the second type the amount of electron donor is twice as much as electron acceptor (m=2)In other cases in which m is greater than 2, the resulting copolymer is an alternating block copolymer [28].

Table 3-3 shows the behavior of instantaneous copolymer composition in different flow regimes, in the absence and in the presence of static mixer. In Table 3-3-a, shows this behavior for emulsion copolymerization in the absence of static mixer. As it can be seen, with 95 wt % of vinyl acetate in feed, instantaneous copolymer composition has a maximum in turbulent flow. The product in laminar flow is rich of butyl acrylate and poor of vinyl acetate. In laminar-turbulent , turbulent , and highly turbulent flow the product is an alternating block copolymer which differs in vinyl acetate sequence length. With feed contains 85 wt % vinyl acetate, fluid velocity has less effects on instantaneous copolymer composition. The product is an alternating copolymer with vinyl sequences smaller than that of previous case. With feed containing 75 wt % vinyl acetate, however, fluid velocity is less effective than previous case on the variation of instantaneous copolymer composition. Here, the products are mostly an alternating copolymer.

Table 3-3-b shows the behavior of instantaneous copolymer composition in different flow regimes at the presence of static mixer. With the feed containing 95 wt % of vinyl acetate, instantaneous copolymer composition has a sinusoidal behavior. It starts to increase in laminar flow and reaches to a maximum in laminar turbulent flow region. It decreases in turbulent flow , then increases in highly turbulent flow. In all regions the final copolymer is an alternating block one which differs in the length of vinyl acetate segments, but in most cases they are smaller than that the one produced in the absence of static mixer. With 85 wt % vinyl acetate in feed instantaneous copolymer composition has a maximum in turbulent flow. In laminar flow and highly turbulent flow the product is an alternating copolymer, and in laminar turbulent transition and turbulent flow region an alternating block copolymer is made. With 75 wt % vinyl acetate in feed, instantaneous copolymer composition has a limited sinusoidal behavior. in all regions the copolymer is an alternating one.

In general with increasing the amount of butyl acrylate in feed, the vinyl acetate sequences become smaller and the structure of copolymer tends to become alternating rather than alternating blocks.

Table 3-3: Instantaneous copolymer composition (ICC) as a function of Reynolds number in emulsion copolymerization of vinyl acetate-butyl acrylate (a) without static mixer (b) using static mixer.

(a)

	ICC in different vinyl acetate-butyl acrylate ratios		
Re	95/5	85/15	75/25
6500	0.47	1.60	2.17
7500	20.55	1.67	1.64
8600	30.30	1.69	1.44
9700	8.04	4.89	2.69

(b)

	ICC in different vinyl acetate-butyl acrylate ratios		
Re	95/5	85/15	75/25
6500	2.87	1.75	.98
7500	6.10	2.52	1.54
8600	4.89	4.88	1.08
9700	5.77	1.74	1.57

3.8 Conclusion

Emulsion copolymerization of vinyl acetate and butyl acrylate was done in a tubular reactor. Effect of static mixer is investigated on the conversion, particle size , and copolymer composition of the product. It was found that maximum conversion obtained depends on the butyl acrylate in feed content and also the presence or the absence of static mixer. By increasing butyl acrylate in the feed maximum conversion decreases. Static mixer , in general decreases the conversion in all condition, because it applies a high shear on the micelles monomer swollen particles and destroyed them.. Also, static mixer has a strong effect on the evolution of particle size distribution, instantaneous copolymer composition , and the structure of final copolymer, alternating copolymer or alternating block copolymer. Secondary nucleation observed during the emulsion copolymerization. By increasing butyl acrylate in the feed, secondary nucleation decreases. Mean particle size in all cases decreased during the time and reached to an approximately constant level. Copolymer composition has a unique behavior for each recipe. It is observed that ,in each flow region, decreasing the amount of vinyl acetate in feed, vinyl acetate content in copolymer decreased, as expected. Increasing the amount of butyl acrylate in feed causes to shorten vinyl acetate sequence length in copolymer and the latex tends to become an alternating copolymer This is true, also, in presence of static mixer. In general, in tubular reactor, in absence or presence of static mixer, the structure of copolymer can be controlled and one can obtain an alternating copolymer in this kind of reactor.

3.9 Acknowledgment

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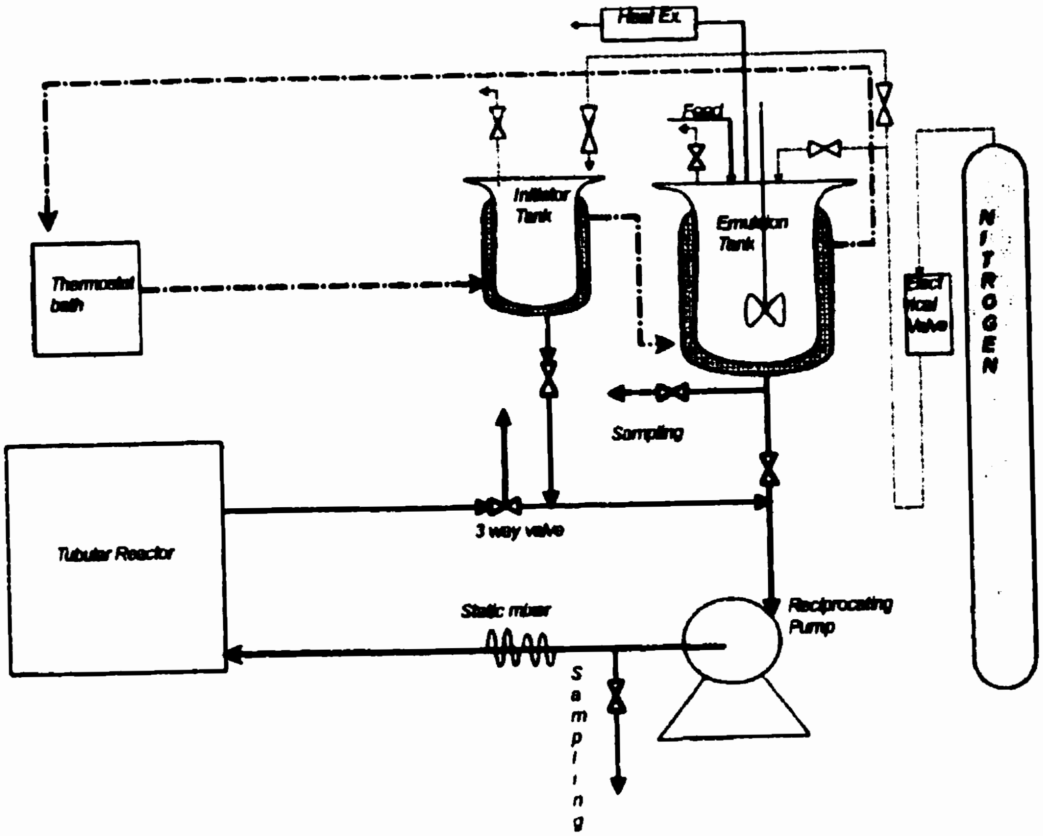


Figure 3-1: **Reactor Design**

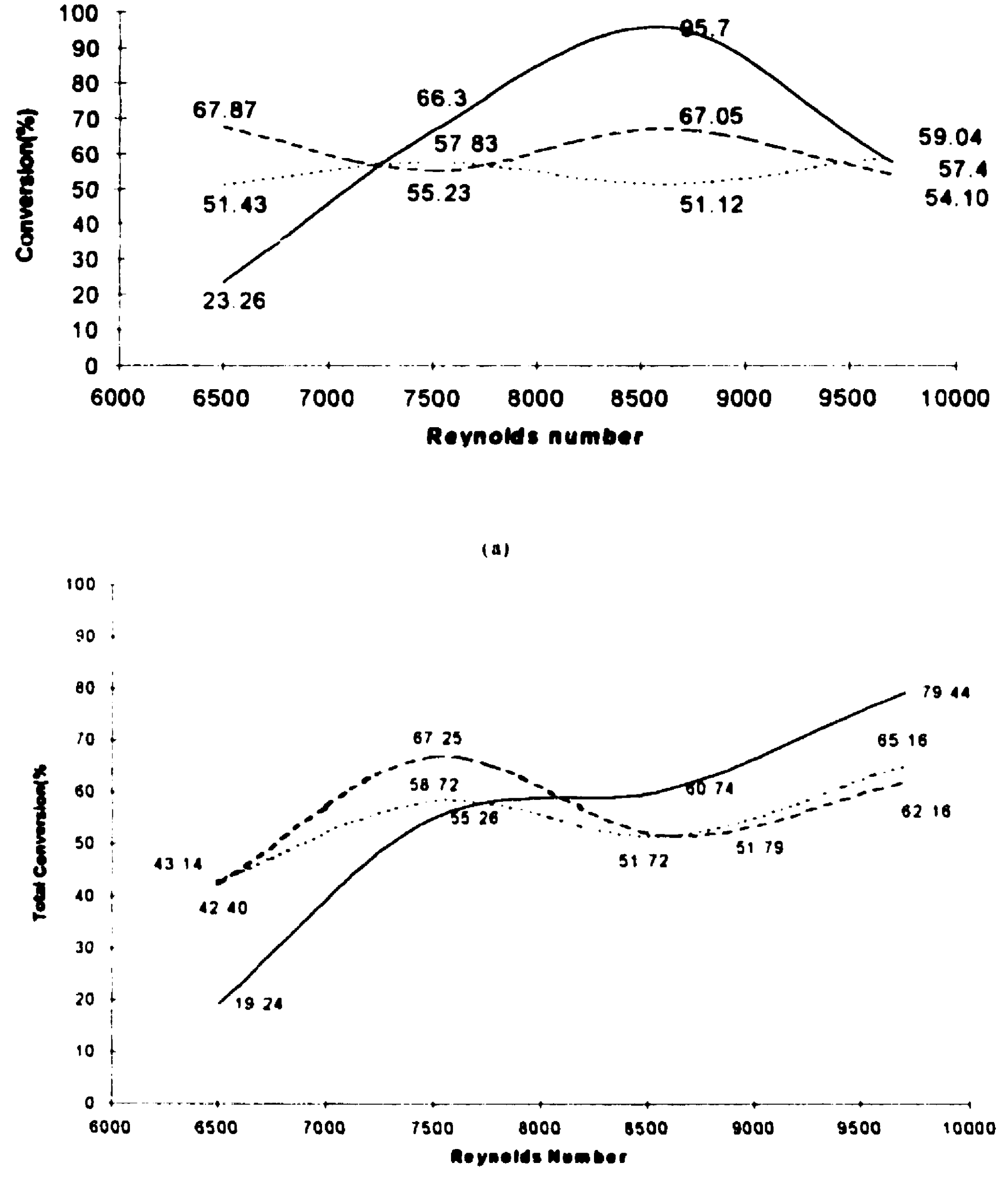


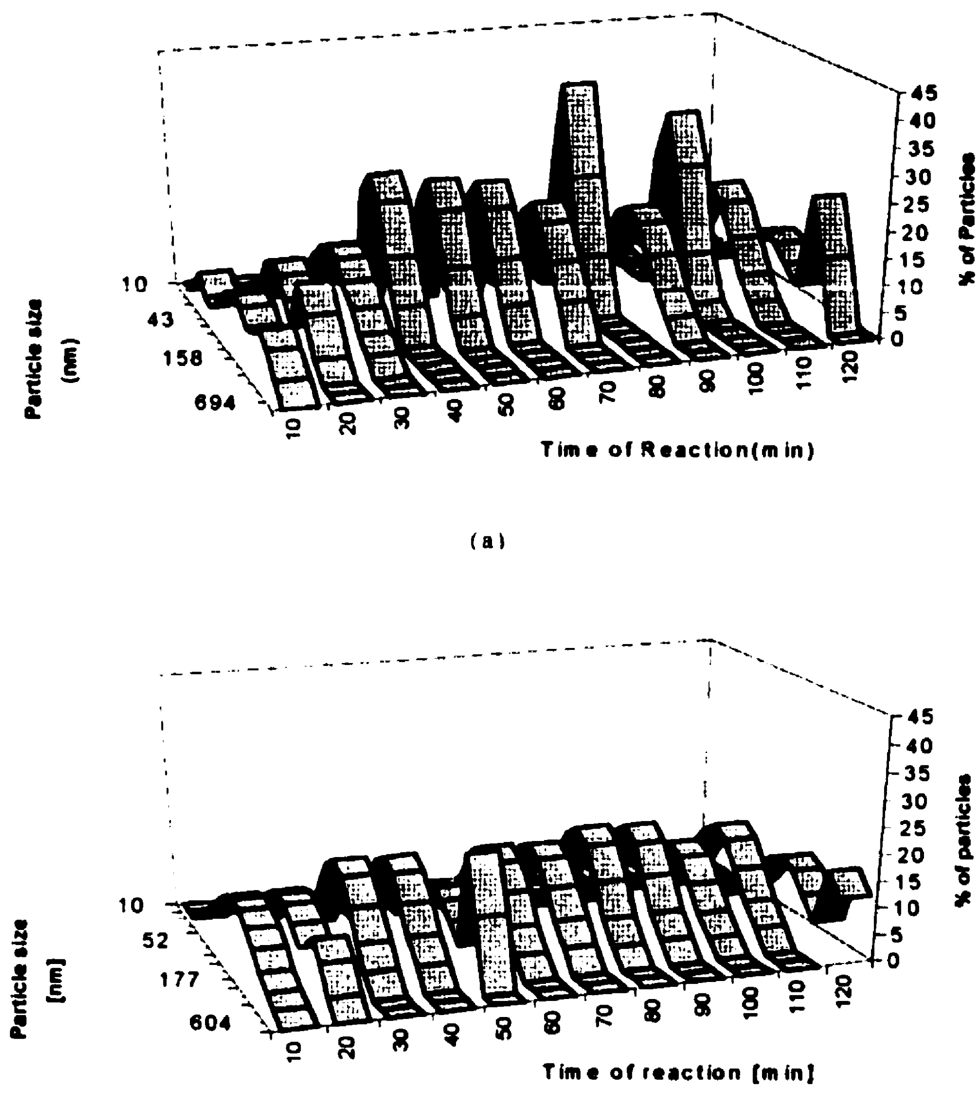
Figure 3-2 : Total conversion as a function of Reynolds number in the emulsion copolymerization of vinyl acetate and butyl acrylate;

a) Reaction at presence of static mixer

Vinyl acetate -Butyl acrylate ratios: (———) 95/5, (………) 85/15, (- - - - -) 75/25

(b) Reaction at presence of static mixer

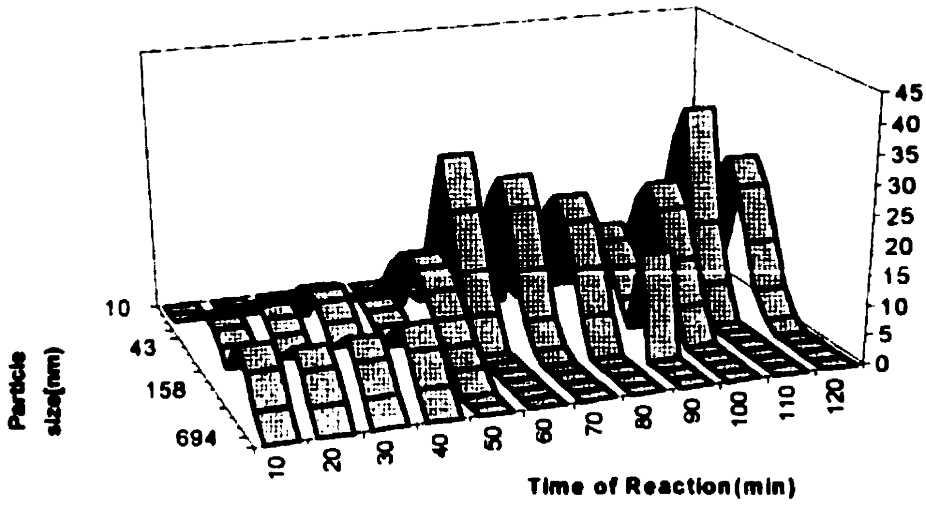
Vinyl acetate -Butyl acrylate ratios: (———) 95/5, (- - - - -) 85/15, (………) 75/25



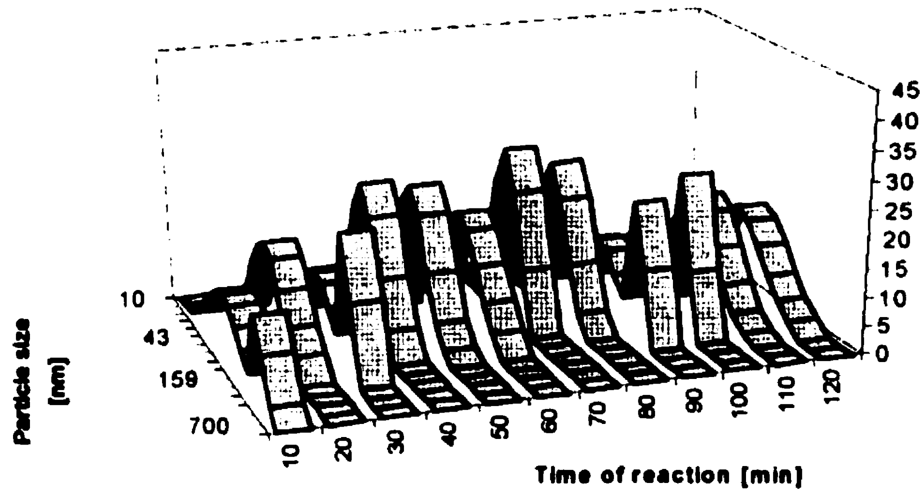
(a)

(b)

Figure 3-3: The evolution of particle size distribution in emulsion copolymerization of vinyl acetate- butyl acrylate with 95 wt % vinyl acetate and 5 wt % butyl acrylate in feed, (a) without static mixer, (b) using static mixer



(a)



(b)

Figure 3-4: The evolution of particle size distribution in emulsion copolymerization of vinyl acetate- butyl acrylate with 85 wt % vinyl acetate and 15 wt % butyl acrylate in feed, (a) without static mixer, (b) using static mixer

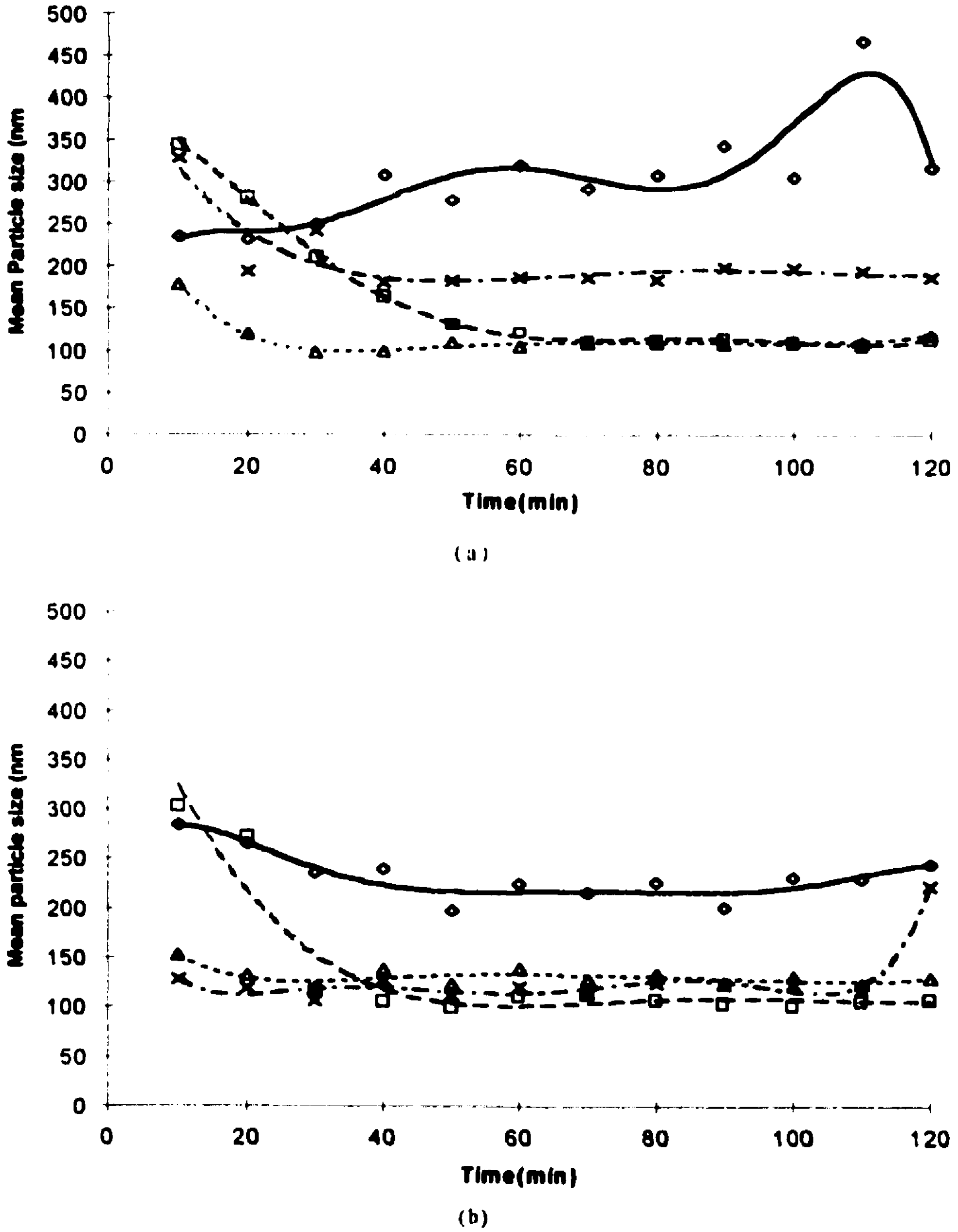


Figure 3-5: Effect of flow rate on the evolution of mean particle size in emulsion copolymerization of vinyl acetate- butyl acrylate with 95 wt % vinyl acetate and 5 wt % butyl acrylate in feed,

a) without static mixer, (O) Re = 6500, (□) Re = 7500, (◇) Re = 8600, X) Re = 9700

(b) using static mixer, (O) Re = 6500, (□) Re = 7500, (◇) Re = 8600, (X) Re = 9700

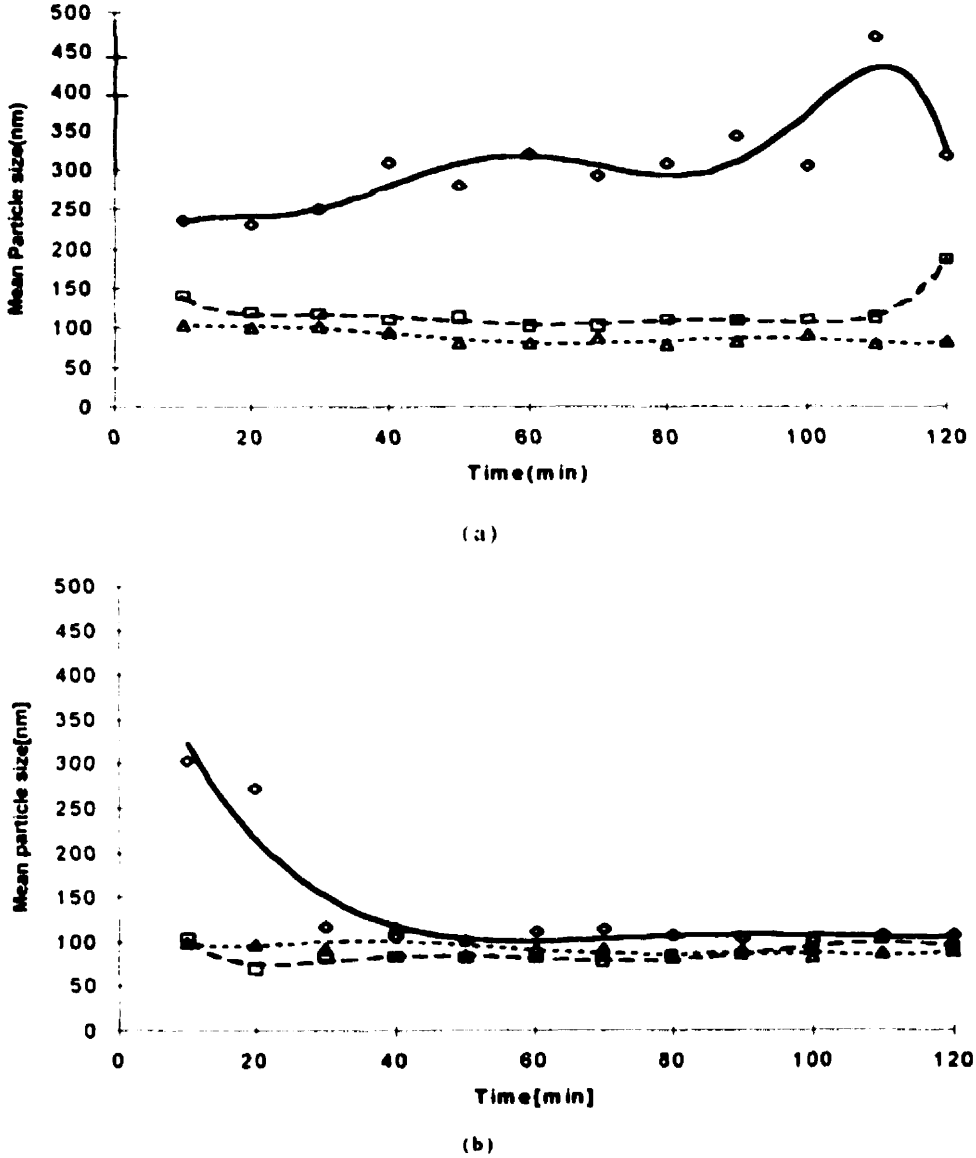


Figure 3-6: Effect on monomers composition in feed on the evolution of mean particle size in emulsion copolymerization of vinyl acetate- butyl acrylate

(a) without static mixer, Re=6500,
(◇) 95 wt% vinyl acetate, 5 wt% butyl acrylate, (□) 85 wt% vinyl acetate, 15 wt% butyl acrylate, (△) 75 wt% vinyl acetate, 25 wt% butyl acrylate.
(b) using static mixer, Re=6500
(◇) 95 wt% vinyl acetate, 5 wt% butyl acrylate, (□) 85 wt% vinyl acetate, 15 wt% butyl acrylate, (△) 75 wt% vinyl acetate, 25 wt% butyl acrylate.

CHAPTER 4 : A COMPARATIVE STUDY ON COPOLYMER COMPOSITION IN THE EMULSION COPOLYMERIZATION OF VINYL ACETATE -BUTYL ACRYLATE IN A TUBULAR REACTOR

Reference:

Poormahdian, S., Bataille, P. "A Comparative Study on Copolymer Composition In The Emulsion Copolymerization Of Vinyl Acetate -Butyl Acrylate In A Tubular Reactor", To be published in the Journal of applied polymer science (March 1999)

Keywords :

emulsion polymerization, copolymerization, vinyl acetate, butyl acrylate, reactivity ratio

4.1 Context[2]

In chapter 3 it is shown that static mixer has a strong effect on the final conversion, particle size distribution, and copolymer composition of the final latex. In this the reactivity ratio of emulsion copolymerization is under investigation, and the results will be compared together with those obtained in batch and tubular reactor operating with static mixer.

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[2] This section in not included in the original manuscript. It only serves as a transition between papers of the thesis.

4.1 Synopsis

Emulsion copolymerization of vinyl acetate and butyl acrylate was carried out in a tubular reactor. Experiments were done in the reactor with normal configurations and some of them in presence of a static mixer at the same conditions.

In this work the apparent reactivity ratio of vinyl acetate with butyl acrylate were determined at different flow regions and it was compared with the one was determined in a batch reactor and the ones determined in a tubular reactor equipped with a static mixer. It was found that copolymer composition in a tubular reactor for each recipe has a unique behavior which is different from each other, as well as those obtained in a batch reactor. Effect of flow rate was investigated on conversion and copolymerization rate. It was found that in each flow region, variation of mole fraction of vinyl acetate in copolymer (F_1) as a function of mole fraction of vinyl acetate in feed (f_1) has a unique behavior. Type and shape of reactor (batch or continuous), and flow rate and static mixer have strong effect on the apparent reactivity ratios of monomers in the emulsion copolymerization. The flow velocity has a strong effect on the apparent reactivity ratios of vinyl acetate and butyl acrylate. In tubular reactors, the reactivity of two monomers depends on the nature of monomers, the fluid velocity and the presence of a static mixer . Also it was found that flow rate and feed's monomer composition have little effect mole fraction of vinyl acetate in copolymer.

4.2 Introduction

Emulsion copolymerization is a heterogeneous reaction process in which unsaturated monomers or monomer solutions are dispersed in a continuous phase with the aid of an emulsifier system and polymerized with a free-radical or a redox initiator systems. Emulsion polymerization is one of the important technique for the commercial production of polymers. The chemistry involves free-radical reactions which are common to many bulk, solution,, and suspension polymerization systems, but the physical degree of subdivision of the reaction mixture in the colloidal size range can have a pronounced influence on the progress of polymerization and the characteristics of the product and its performance.

Mark[1], for the first time used a tubular reactor, Calcott and Starkweather[2] improved the reactor. Emulsion copolymerization of styrene and butadiene was done by Feldon et al.[3] in laminar flow. A plug flow reactor (PFR) was used to produce seed particles for a CSTR by Ueda et al.[4]. Ghosh and Forsyth[5] used a tubular reactor for polystyrene and formulated a model. Rollin et al.[6] discussed the influence of Reynolds number on the rate of polymerization of polystyrene in a closed-loop reactor. Vatanatham and Forsyth[7] studied emulsion copolymerization of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) in a tube. Rollin et al.[8] , for the first time, used a helical reactor in open loop. Lynch and Kiparissides[9] simulated the turbulent experiments of Rollin et al[6]. Lee and Forsyth[10] considered the seeded polymerization of vinyl acetate in the reactor built by

Vatanatham and Forsyth[7]. Bataille et al.[11] investigated the copolymerization of styrene and α-methyl styrene in an open loop reactor. Lee and Poehlein[12] used a Teflon coated tubular reactor as a seed reactor for a CSTR. Shoaf and Poehlein[13] worked the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR, and tubular reactors. Bataille and Dalpé[14] studied the polymerization of vinyl acetate in a closed loop reactor. Lee et al.[15] investigated the polymerization of styrene in a continuous recycle reactor. Iabbadène and Bataille[16] analyzed the emulsion polymerization in a pulsed tubular reactor.

No work, however, was reported on the effect of static mixer or the liquid flow on the apparent reactivity ratios in the emulsion copolymerization of vinyl acetate-butyl acrylate in a tubular reactor. This is the object of this paper.

4.3 Reactor Geometry

Most of the studies mentioned here have all been done in essentially straight tubular reactors, the curved parts (the elbows) constituted only very small proportion of the total length. A reactor of commercial interest operated to a Reynolds number in the vicinity of 2100 would be on the order of 60 to 600 meters in length depending on the tube diameter. The advantage of good heat transfer and temperature control of emulsion polymerization are generally realized by the immersion of the reactor in a heat transfer medium of substantial thermal capacity. This is difficult and costly to achieve with a linear tubular reactor in used and a helical configuration suggests itself as a viable alternative. According to the works of Eustice[17], Dean[18], Taylor[19], and Srinvasan[20] the curvature of tube decreases flow perturbations and increase the value of the Reynolds number at which the laminar- transition occurs. Iabbadène[21] calculated this critical Reynolds number in the vicinity of 7500 and in this work this calculation was used as a basis to design the reactor and operation.

4.4 Experimental

4.4.1 Tubular Reactor

All experiments were done in a tubular reactor shown in Figure 4- 1. This system consists of an emulsion tank, an initiator tank, a purging system, a heat exchanger, a tubular reactor, a reciprocating pump , a static mixer, and a data acquisition system. Emulsion tank with a capacity of 3 L, jacketed and equipped with a pitch blade (P-6) impeller ,and four vertical baffles with 10 mm in width, 200 mm in length, 1 mm clearance to help better mixing. Initiator tank a capacity of 1L, it is also jacketed. Each tank had openings for thermocouples, feeding, nitrogen inlet, mixer shaft and for a heat exchanger.

Thermostat bath is a cylindrical glass vessel that is used to heat the jacketed vessel to reach the desired temperature.

Tubular reactor is a 5 meter Teflon-lined tube,2.23 cm inside diameter, surrounded by a stainless steel mesh 43 cm coiled, placed in a thermostat bath, equipped with a static mixer and a calibrated reciprocating pump. The reciprocating pump permits to change the velocity of the circulating fluid, by changing the pump speed. Temperatures of different sites of the system are recorded by means of a data acquisition system. Each part of the system can be purged separately with nitrogen.

4.4.2 Materials

Inhibited monomers, vinyl acetate(Vac) and butyl acrylate (BuA) and the other materials were used as received. The general formulations used are given in **Error! Reference source not found.**.

Table 4-1: Recipes used in experiments based on 100 parts of vinyl acetate and butyl acrylate

Material	Recipe 1	Recipe 2	Recipe 3
Vinyl acetate(monomer)	95	85	75
Butyl acrylate(monomer)	5	15	25
Distilled water	321.8	321	324.7
Sodium Lauryl sulfate(surfactant)	1.75	1.75	1.75
Potassium Persulfate(initiator)	0.24	0.24	0.24
NOPCO(Antifoaming agent)	10 drops	10 drops	10drops

4.4.3 Procedure

The emulsifier was dissolved in 1000mL of distilled water together with 10 drops of NOPCO as an antifoaming agent. The initiator was dissolved in 200mL distilled water. All parts of the system including tubes, emulsion tank, and initiator tank, were purged with nitrogen. The solution of emulsifier, and the required amounts of vinyl acetate, butyl acrylate and 1500mL of distilled water were poured inside the emulsion tank. Emulsification was performed using the mixer, and continued for 50 minutes to make sure the emulsification is complete. The emulsion was then transferred to the tube. The reciprocating pump was turned on and set at the highest speed in order to reach quickly 60 °C. This took between 15 to 25 minutes depending on the recipe. When the temperature in the tube reached 60 °C, the pump was set at the desired speed to obtain the required Reynolds number. The liquid was mixed for about 30 minutes so that it reaches a constant velocity profile. After this period, the warmed up initiator solution was injected inside the tube by means of nitrogen exerted through the initiator tank. This is considered as t=0 for the emulsion copolymerization. The copolymerization continued to proceed for up to 2 hours. During the reaction, samples were collected through the sampling valve and the reaction short-stopped with hydroquinone. Finally the pump was turned off and the produced latex was discharged through the sampling valve, then the three-way valve was opened and all the system was washed with water.

Collected samples were analyzed for conversion, particle size distribution and copolymer composition. Particle size distribution was measured by using a laser light scattering from Brookhaven Instruments Corporation, connected to a BIMODAL-203AT digital correlator, where the data could be collected. For this analysis, dust-free doubled distilled water was used. The measurements were carried out by maintaining the samples in a paraffin bath at 25 °C . The data obtained from this instrument processed to have a distribution curve based on the fraction of particles.

A Brucker WH400 spectrometer (400.13 MHz) was used to obtain the molar composition of latex by NMR spectra. Knowing the CH group resonance in vinyl acetate (5.22 ppm) and -O-CH_2 group resonance in butyl acrylate (4.13 ppm), the composition was calculated from the area under each peak[22].

Reynolds numbers of 6500, 7500, 8600, and 9700 were applied to each set of experiments. The reciprocating pump was calibrated with water at 60 °C.

4.5 Results And Discussion

4.5.1 Study On The Copolymer Composition Curve

4.5.1.1 In Absence Of Static Mixer

Instantaneous copolymer composition is defined by equation (1) and it is related to the reactivity ratios by the copolymer composition in equation (2)[23]. In this equation r_1 and r_2, reactivity ratio of vinyl acetate and butyl acrylate in the system vinyl acetate-butyl acrylate , respectively, are 0.024 and 10.67[22]. Figure 4-2 shows the copolymer composition of this system based on equation 4.1.

$$m = \frac{d[M_1]}{d[M_1]+d[M_2]} \qquad (4\text{-}1)$$

$$F_1 = \frac{r_1 . f_1^2 + f_1 . f_2}{r_1 . f_1^2 + r_2 . f_2^2 + 2 f_1 . f_2} \qquad (4\text{-}2)$$

This relation is defined for batch reactors. In regard with the data obtained from N.M.R. the curve of mole fraction of vinyl acetate in copolymer (F_1) could be plotted as a function of mole fraction of vinyl acetate in feed (f_1) for continuous reactors and the data compared with those calculated from equation (1). Only the values over 80 mole % vinyl acetate in feed are shown and for comparison only the upper part of Figure 4-3 is shown. In Figure 4-2 it can be seen that in batch reactors, by increasing vinyl acetate in feed, mole fraction of vinyl acetate in copolymer sharply increased. The diagonal line shows the azeotropic points where mole fraction of vinyl acetate in feed is the same as that of the copolymer. As Figure 4-2 shows in batch reactors emulsion copolymerization of vinyl acetate and butyl acrylate is far from being azeotropic. In Figure 4-3 copolymer composition (F_1) is plotted as a function of f_1 for the system vinyl acetate-butyl acrylate at different Reynolds numbers. It can be seen that for each flow region the polymerization has a unique behavior. In laminar flow (Re=6500) it has a minimum at 97 mole % then behaves as in a batch reactor. In laminar-turbulent transition flow (Re=7500) an interesting result is observed. By increasing the mole fraction of vinyl acetate in feed the copolymer composition is increased and at $f_1=0.98$ lies on the diagonal line to $f_1=1$. It means that it could be possible to have a polymerization which will react as an azeotrope in this area. In turbulent flow (Re=8600) the curve has an azeotrope at $f_1=0.97$. Before the azeotrope mole fraction of vinyl acetate in the copolymer is less than that in the feed. After the azeotrope, mole fraction of vinyl acetate in the feed is less than in the copolymer. This behavior is seen in systems such as styrene- methyl methacrylate . In this system the reactivity ratios of styrene and methyl methacrylate are, respectively, $r_1=0.53$ and

r_2=0.56[23] which are very close to each other[24]. In highly-turbulent flow (Re=9700), the behavior changes continuously , but nothing to be compared to the batch process. Based on above description it could be summarized that type and shape of reactor (batch or continuous), and flow rate have strong effect on the apparent reactivity ratios of monomers in the emulsion copolymerization. The level of composition drift is also a function of these factors. It is possible to find r_1 and r_2 from copolymer composition curve, equation 2. The slope at f_1=1 gives $\frac{1}{r_1}$. The r_1 and r_2, obtained from the method described elsewhere[22] in different flow regions are summarized in Table 4-2.

Table4-2: The values of r_1 and r_2 for batch and tubular reactor

Type	r_1 Vinyl acetate	r_2 Butyl acrylate	$\frac{r_2}{r_1}$
Batch	0.024	10.67	444
Re=6500 (laminar flow)	.078	10.47	134
Re=7500 (laminar-turbulent transition flow)	1	17.04	17.0
Re=8600 (turbulent flow)	2.69	47.83	17.8
Re=9700 (highly-turbulent flow)	0.38	0.45	1.2

It can be seen from Table 4-2 that r_1 and r_2 have different values in different flow conditions. This shows that in tubular reactors, reactivity of the two monomers depends on the nature of monomers, and flow regions (laminar, transition, turbulent, or high turbulent flow). By adjusting the proper flow conditions i.e. reactivity ratios one can obtain a copolymer with a specific structure .

4.5.1.2 In Presence Of The Static Mixer

In Figure 4-4 is plotted F_1 (mole fraction of vinyl acetate in copolymer) versus f_1 (mole fraction of vinyl acetate in feed) in presence of a static mixer - In this Figure ,as in the previous section, due to the limitations of the experiments only the values of over 80 mole % vinyl acetate in feed are shown and as a reference only the upper part of Figure 4-2 is shown. For each flow region this curve has a unique behavior. In laminar flow , by increasing f_1, F_1 increases. In this case composition drift is always less than that in batch reactors. Composition drift is the difference between the experimental F_1 and that of the value from the diagonal line. In laminar-turbulent transition flow, an increase in f_1 causes also an increase in F_1, but the composition drift is less than that in the previous case. In turbulent flow , F_1 has the same behavior as before. In highly-turbulent flow , with $f_1=0.98$, F_1 lies on a diagonal line suggesting an azeotropic composition in this point. Based on the above description it could be said that in addition to the type and shape of reactor (batch or continuous) and flow rate , the existence of a static mixer in the tubular reactor has strong effect on the apparent reactivity ratio of participating monomers in the emulsion copolymerization. A comparison of the column related to r_1 and r_2 in Table 4-2 and 3 shows that presence of static mixer caused to increase of r_1 in laminar flow and highly-turbulent flow and decrease that in laminar-turbulent transition flow and turbulent flow. Also the static mixer causes to decrease r_2 in all flow regions except highly-turbulent flow. A comparison of the columns related to r_1 and r_2 in Table 4-2 and 4-3 shows that the presence of static mixer caused to increase r_1 in laminar flow and highly-turbulent flow, and decrease of that in laminar-turbulent transition flow and turbulent flow. Also static mixer caused to decrease r_2 in all flow regions except highly-turbulent flow. This comparison showed the ratio $\frac{r_2}{r_1}$ in all flow regions has a smaller value in presence of static mixer except in highly-turbulent flow. The level of composition drift is also a function of these factors. This is also obtained in case of emulsion copolymerization in the absence of static mixer. The reactivity ratios of vinyl acetate and butyl acrylate in different flow regions are summarized in Table 4-3.

Table4-3: The values of r_1 and r_2 for batch and tubular reactor (equipped with a static mixer)

Type	r_1 Vinyl acetate	r_2 Butyl acrylate	$\frac{r_2}{r_1}$
Batch	0.024	10.67	444
Re=6500 (laminar flow)	0.15	7.01	46.7
Re=7500 (laminar-turbulent transition flow)	0.43	2.458	5.7
Re=8600 (turbulent flow)	0.36	2.641	7.34
Re=9700 (highly-turbulent flow)	1	15.394	15.4

It is clear from Table 4-3 that r_1 and r_2, like in the previous case, have different values in various flow regions. This shows that in a tubular reactor, reactivity of the two monomers depends on the nature of monomers. The existence of static mixer has a major effect on the polymerization as it reduces the reactivity ratio of vinyl acetate in laminar flow , transition and turbulent flow, and increases in highly-turbulent flow .

4.5.2 The Effect Of Flow Rate (Reynolds Number) On Total Conversion As A Function Of Mole Fraction Of Vinyl Acetate In Copolymer

One of the important factors to distinguish the structure of a copolymer is the plot of final conversion as a function of copolymer composition[25]. With this plot it is possible to know if a polymer is rich or poor in vinyl acetate. The three monomer compositions in feed is sketched in Figure 4-(5-a, 5-b, 5-c). Figure 4-5 shows that, in all feed compositions ,inspite of the difference in flow rates all curve evolve the same way and have little deviation. Similar curves are obtained for copolymerization in presence of a static mixer.

4.5.3 The Effect Of Feed's Monomer Compositions

It is observed that in all cases, by increasing butyl acrylate in feed, an increase in vinyl acetate content of copolymer causes an increase in the conversion rate. This is shown in Figure 4-(6-a,6-b,6-c,6-d) for emulsion copolymerization in absence of static mixer and in Figure 4-(7a-7d) for emulsion copolymerization in presence of a static mixer. This is due to the fact that in at a given mole fraction of vinyl acetate in feed the behavior of this curve is independent of flow rate.

4.6 Conclusion

Emulsion copolymerization of vinyl acetate and butyl acrylate was carried out in a tubular reactor. Experiments were done in the reactor normal configuration and also when equipped with a static mixer. In this work copolymer composition and apparent reactivity ratio of the copolymer was under investigation. It was found that copolymer composition in a tubular reactor for each recipe has a unique behavior which is different from each other, as well as those obtained in a batch reactor. An azeotropic point was observed in laminar-turbulent transition flow. Type and shape of reactor (batch or continuous), and flow rate have strong effect on the reactivity ratios of monomers in the emulsion copolymerization. The level of composition drift is also a function of these factors. Reactivity ratios, r_1 and r_2 has different values in different flow conditions. It means that the reactivity of the two monomers depends on the nature of monomers, and flow velocity. By adjusting the proper flow conditions one can obtain a copolymer with a specific structure. Static mixer can reduce the composition drift, even less than that in batch reactors. It has, however, a major effect on the polymerization as it reduces the apparent reactivity ratio of vinyl acetate in laminar flow, laminar-turbulent transition flow, and turbulent flow, and increases in highly-turbulent flow. Also it was found that flow rate and feed's monomer composition have little effect on mole fraction of vinyl acetate in copolymer (F_1) at a certain conversion in different flow regions.

4.7 Acknowledgment

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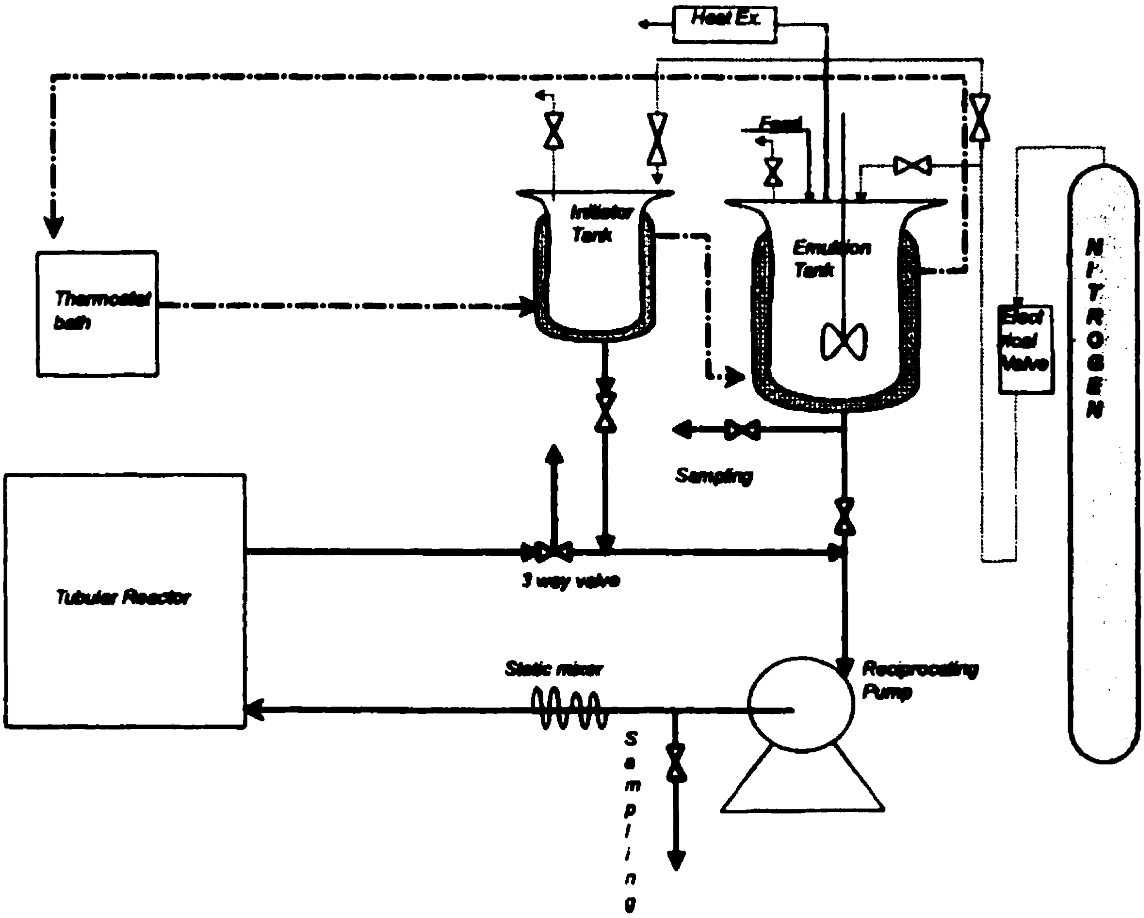


Figure 4-1: Reactor Design

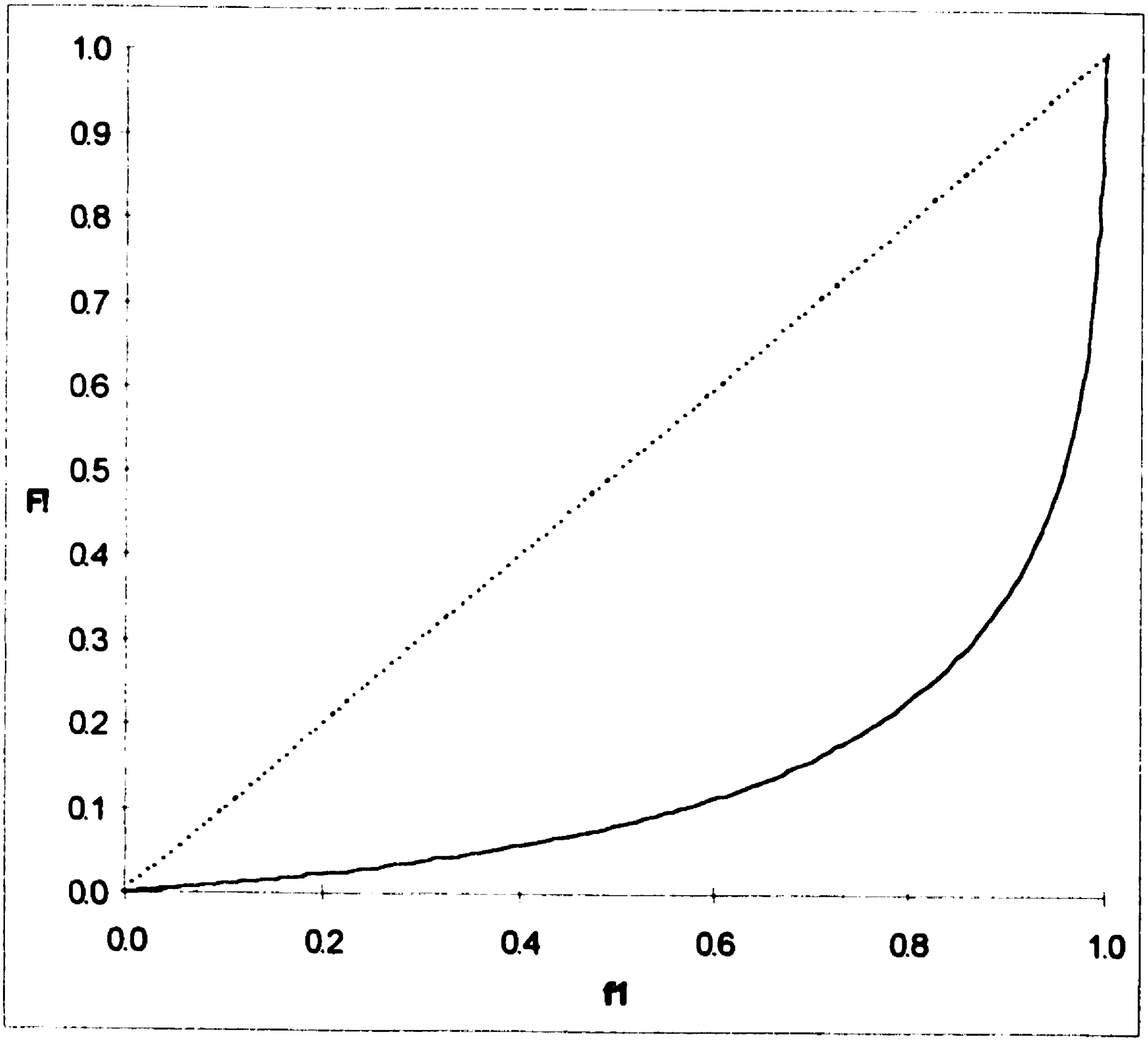


Figure 4-2: F1 mole fraction of vinyl acetate in polymer formed where f1 is the mole fraction of vinyl acetate in feed

(············) Azeotropic line, (————) mole fraction of vinyl acetate in polymer

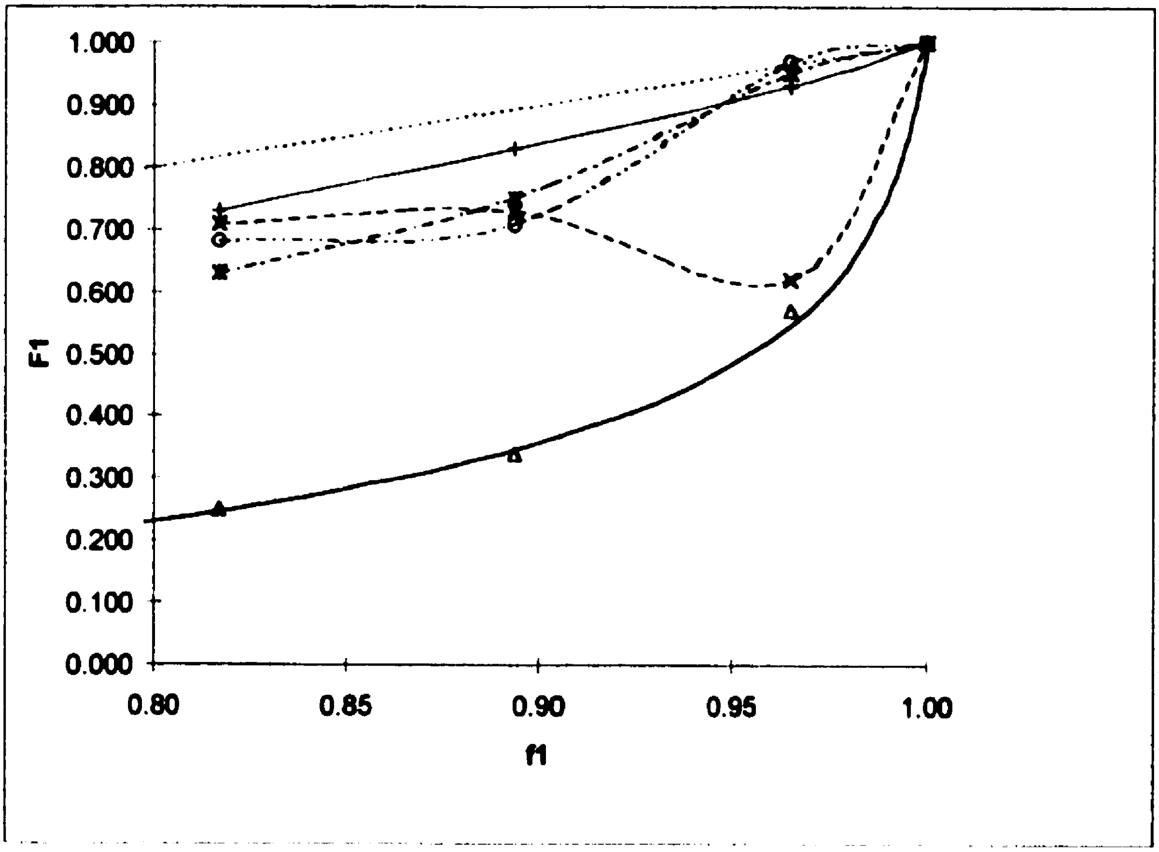


Figure 4-3: Copolymer composition curve of emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor in different Reynolds numbers

(Δ) Calculated, (×) Re = 6500, (✱) Re = 7500, (○) Re = 8600, (+) Re = 9700

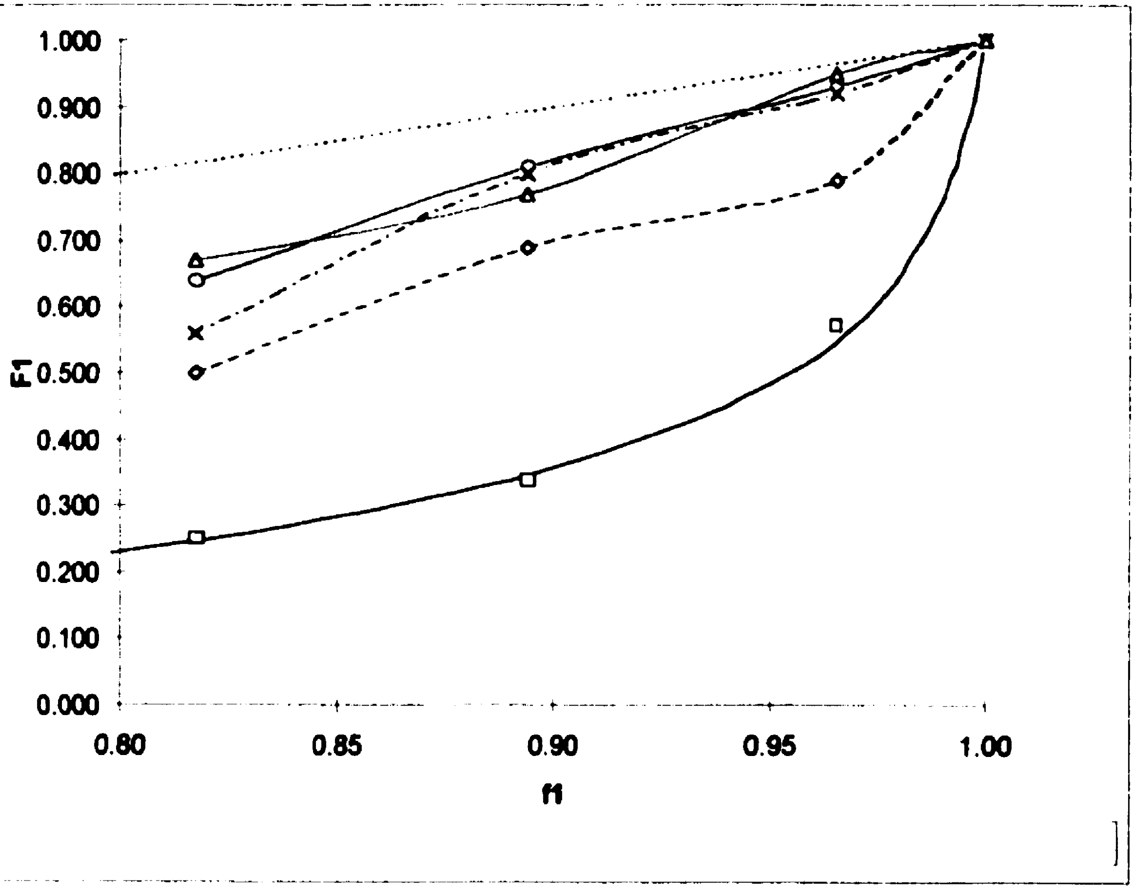


Figure 4-4:Copolymer composition curve of emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor equipped with a static mixer in different flow regions

(□) Calculated, (◇) Re = 6500, (×) Re = 7500, (○) Re = 8600, (△) Re = 9700

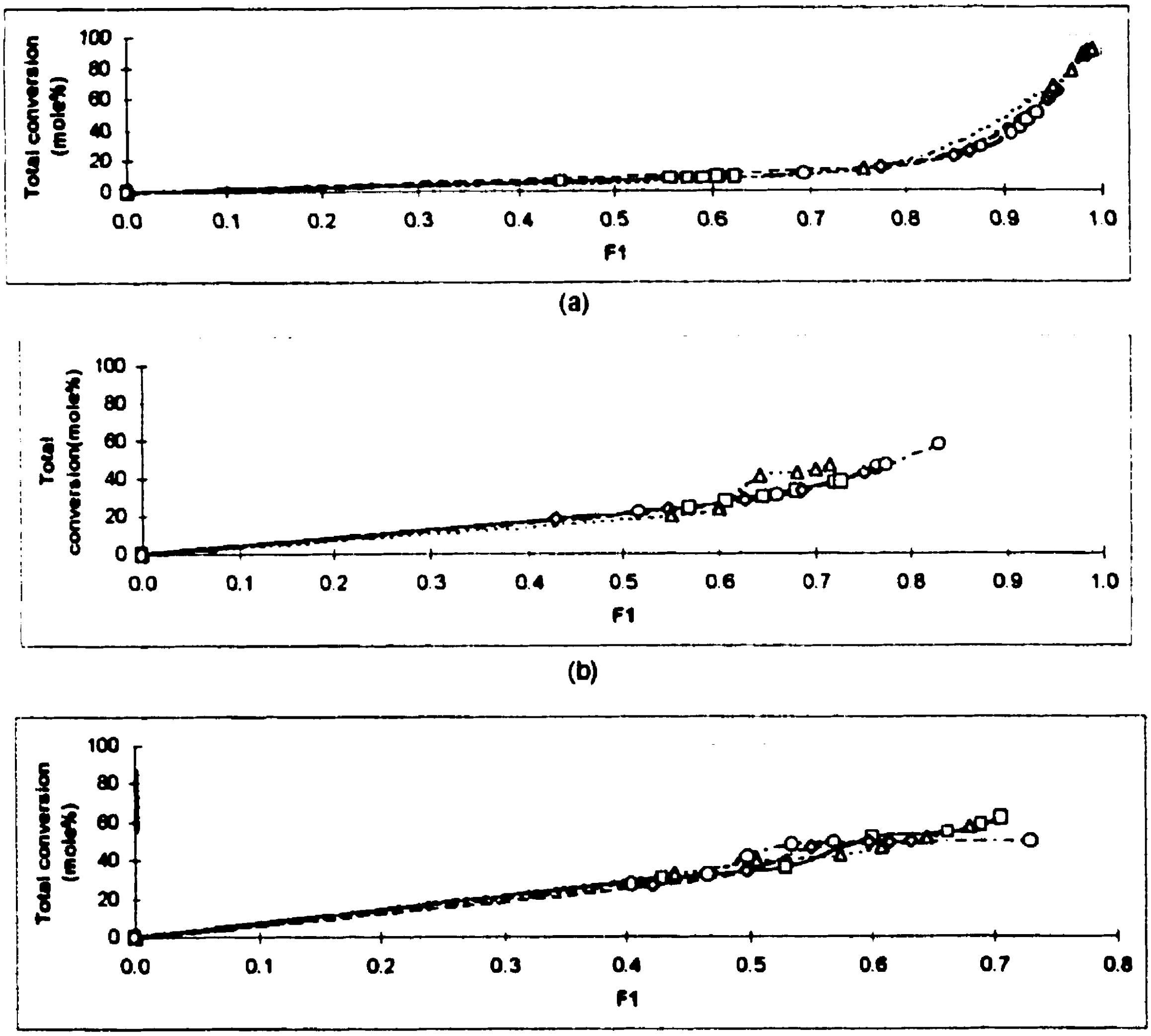
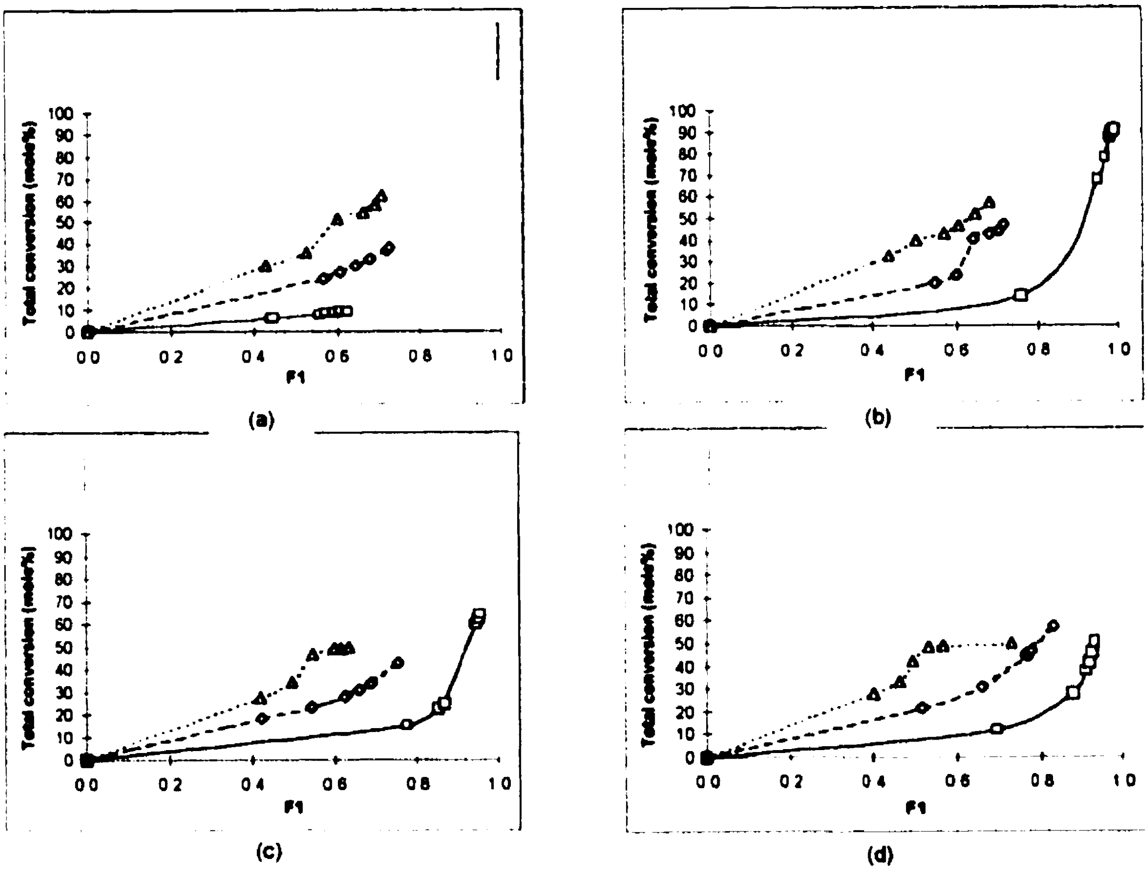


Figure 4-5: Total conversion as a function of vinyl acetate content of copolymer in different flow rates in emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor (a) 95 wt % vinyl acetate and 5 wt% butyl acrylate (b) 85 wt% vinyl acetate and 15 wt % butyl acrylate , (c) 75 wt% vinyl acetate and 25 wt% butyl acrylate

(□) Re = 6500, (◇) Re = 7500, (△) Re = 8600, (○) Re = 9700



(a)

(b)

(c)

(d)

Figure 4-6: Final or total conversion as a function of vinyl acetate fraction of copolymer (F_1) in different flow rates in emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor equipped with a static mixer (a) 95 wt % vinyl acetate and 5 wt% butyl acrylate (b) 85 wt% vinyl acetate and 15 wt % butyl acrylate , (c) 75 wt% vinyl acetate and 25 wt% butyl acrylate

(□) 95 % wt. vinyl acetate, 5 wt% butyl acrylate
(◇) 85 % wt. vinyl acetate, 15 wt% butyl acrylate
(△) 75 % wt. vinyl acetate, 25 wt% butyl acrylate

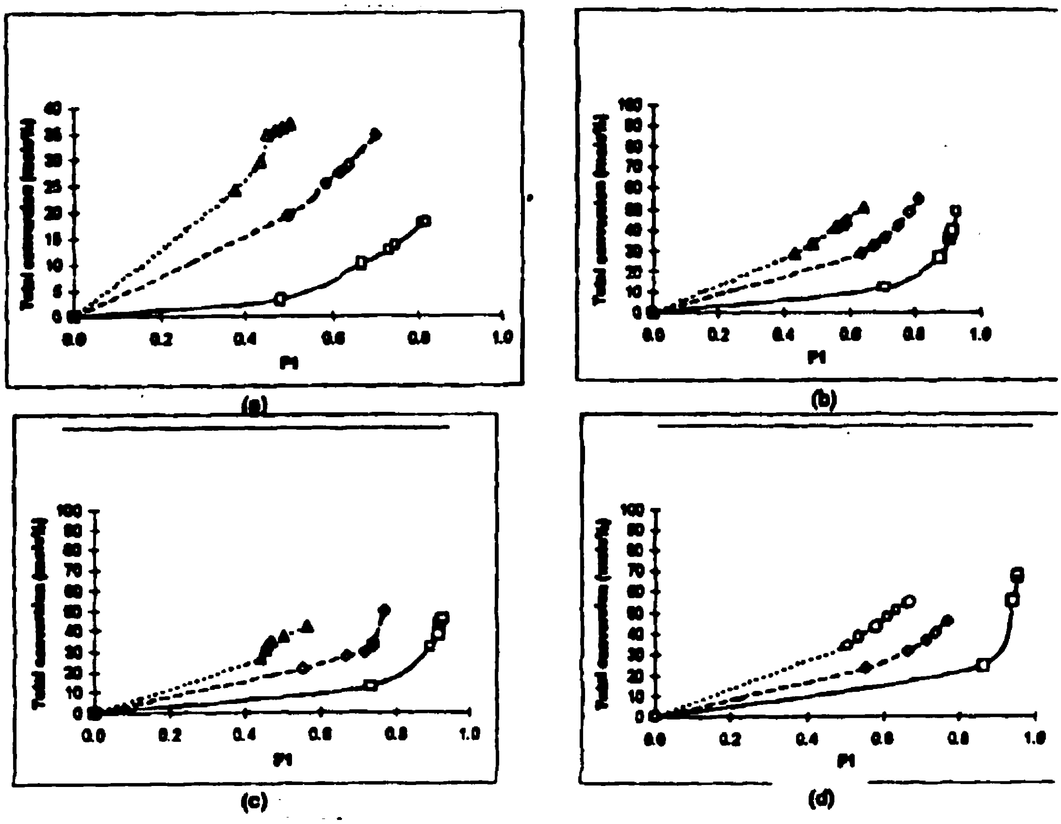


Figure 4-7: Final or total conversion as a function of vinyl acetate content of copolymer in different feed's monomers compositions emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor equipped with a static mixer

(a)Re=6500(laminar flow) (b) Re=7500(laminar-turbulent transition flow)
(c)Re=8600 (turbulent flow) (d) Re=9700 (highly-turbulent flow)
(□) 95 % wt. vinyl acetate, 5 wt% butyl acrylate
(◇) 85 % wt. vinyl acetate, 15 wt% butyl acrylate
(△) 75 % wt. vinyl acetate, 25 wt% butyl acrylate

CONCLUSION

The main objective of the proposed work is to study the copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. Nothing has been covered out for such a system. Specific objectives are as follows: To establish the best conditions using a tubular reactor with and without a static mixer, To evaluate the effect of static mixer on the characteristics of the product, as well as on the particle size distribution in the above systems., To determine the effect of operational parameters on particle size distribution and copolymer composition.

A bench scale tubular reactor was designed and built to investigate the targets of the research.

Emulsion copolymerizations were performed in two different reactor configurations, with and without a static mixer. Many samples were taken during each experiment. These samples were tested for conversion, particle size distribution, and copolymer composition, respectively by gravimetry, Laser Light Scattering, and NMR spectroscopy. For both reactor designs, interesting results were obtained, which confirms that emulsion copolymerization is highly composition, respectively sensitive to the parameters of tthe reactor.

In experiments without static mixer it was found that depending on the monomers composition in feed there is (are) region(s).that conversion is maximum. These regions varies with the feed recipe. It was found also that the amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. Studies on particle size distribution showed that recipes with lower quantities of butyl acrylate have a wide and bimodal particle size distribution in the final latex, and recipes with higher butyl acrylate contents have a narrow and monomodal particle size distribution. So the amount of butyl acrylate and the velocity of fluid flowing inside the tube have strong effects on the shape (monomodal- bimodal) and the width of particle size distributions. This effect may varies with the butyl acrylate content and the fluid velocities. In investigating copolymer composition it was found that an alternative block copolymer is made during the reaction.

In comparing the two different reactor configurations, it was found that maximum conversion depends on the butyl acrylate in feed content and also the presence or the absence of static mixer. By increasing butyl acrylate in the feed maximum conversion decreases. Static mixer , in general decreases the conversion in all condition, because it applies a high shear on the micelles monomer swollen particles and destabilize them. Static mixer has a strong effect on the evolution of particle size distribution, instantaneous copolymer composition , and the structure of final copolymer, alternating copolymer or alternating block copolymer. A Secondary nucleation was observed during the emulsion copolymerization. By increasing butyl acrylate in the feed, the secondary nucleation decreases. Mean particle size in all cases decreased with time to reach a constant level. Copolymer composition has a unique behavior for each recipe. It is observed that ,in each flow region, decreasing the amount of vinyl acetate in feed, vinyl acetate content in copolymer decreases, as expected. Increasing the amount of butyl acrylate in feed causes to shorten vinyl acetate sequence length in copolymer and the latex tends to become an alternating copolymer This is true, also, in presence of static mixer. In general, in tubular reactor, in absence or presence of static mixer, the structure of copolymer can be controlled and one can obtain an alternating copolymer in this kind of reactor.

Finally an analysis was performed on the reactivity ratio of the monomers, vinyl acetate and butyl acrylate, in the tubular reactor. In this analysis it was found that copolymer composition in a tubular reactor for each recipe has a unique behavior which is different from each other, as well as those obtained in a batch reactor. An azeotropic point was observed in laminar-turbulent transition flow. Type and shape of reactor (batch or continuous), and flow rate have strong effect on the reactivity ratios of monomers in the emulsion copolymerization. The level of composition drift is also a function of these factors. Reactivity ratios, r_1 and r_2 have different values at different flow conditions. It means that the reactivity of the two monomers depends on the nature of monomers, and on the flow velocity. By adjusting the proper flow conditions one can obtain a copolymer with a specific structure. Static mixer can reduce the composition drift, even less than that in batch reactors. It has, however, a major effect on the polymerization as it reduces the apparent reactivity ratio of vinyl acetate in laminar flow, laminar-turbulent transition flow, and turbulent flow, and increases in highly-turbulent flow. Also it was found that flow rate and feed's monomer composition have little effect mole fraction of vinyl acetate in copolymer. This may be due to the water solubility of the two monomers. Having a great solubility in water the vinyl acetate is less affected by the break-up of the micelles and thus the relative reactivity ratio well favor more the vinyl acetate as compared to the butyl acrylate.

RECOMMENDATIONS

The following points could be considered valuable in further understanding of governing phenomena in turbulent fluidized bed reactors:

1- The method of monomer addition has a significant effect on the final final conversion and the productivity of the reactor. In this regard, it can be used from starved-monomer addition method for butyl acrylate. There could be an injection rate in which conversion is improved, in comparison with the same conditions but without using this method of addition.

2- By using some kinds of promoters it is possible to increase the final conversion.

3- sure of the effective mixing of initiator in all the emulsion mixture, and ends to start at the reaction throughout the reactor at the same time. Initiator could be injected from different parts of the tubular reactor at the same time.

4- Particle size distribution is a key parameter in all emulsion polymerizations. It is better to determine this parameter soon after sampling. Time needed to collect the samples and preparation method can affect the accuracy of results. It is recommended to use online laser light scattering to determine particle size distribution, during the reaction.

5- Rearange the reactor so that it would be possible to bleed off some emulsion as more reactants are added to the system.

6- Design at the outset of the reactor a separating system were the unconverted material could be recirculated.

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APPENDICES

Appendix I : Calculation Of The Mass Conversion

The following calculation permits to calculate the mass conversion, in percentage, for all experiences of emulsion copolymerization of vinyl acetate and butyl acrylate , done in a semi-continuous reactor.

Since the quantity of monomers presents in the reactor changes with time, it is necessary to determine the present monomers mass to the time where the sample is appropriated. More precisely, it is necessary to calculate the mass fraction of the monomer to the time when the sample is appropriated (a), as well as the mass fraction of surfactant + initiator at the same instant (b).

The formula that gives the mass conversion is:

$$\text{Conversion \%} = \frac{\text{Mass of the dry polymer in the sample}}{\text{Total mass of the sample}} \times 100$$

or

$$\text{Conversion\%} = \frac{(D-A)-b(C-B)}{a(C-B)} \times 100 \qquad \text{(A-1)}$$

where

A = Mass of the empty crystallizer;

B = Mass of the crystallizer + hydroquinone;

C = Mass of the crystallizer + hydroquinone + sample;

D = Mass of the crystallizer + dry sample;

a = mass Fraction of monomers;

b = mass Fraction of surfactant and initiator

c = mass of latex sample = C-B

d = mass Fraction of surfactant and the initiator in the sample of latex = b×c;

e = Mass of the dry residual solids= D -A;

f = Mass of the monomer in the sample of latex = a×c;

g = Mass of the dry copolymer in the sample of latex = e - d;

With these notations, one can write:

$$Conversion\% = \frac{g}{f} \times 100 \tag{A-2}$$

For the calculation of the conversion of the copolymerization in semi-continuous process, the mass fraction of monomers (a) and the mass fraction of surfactant + initiator (b) are calculated of the following way:

$$a = \frac{\text{Mass of monomers at a given instant}}{\text{Mass of reagents in the reactor at this instant}} = \frac{(AV)_t + Q_{av} \times t + Q_{AB} \times t}{m_0 + (AV)_t \times t + Q_{AB} \times t} \tag{A-3}$$

$$b = \frac{\text{Mass of surfactant + initiator}}{\text{Mass of reagents in the reactor at the time t}} = \frac{E}{m_0 + (AV)_i \times t + Q_{AB} \times t} \qquad \text{(A-4)}$$

where

$(AV)_i$ = The quantity of existing vinyl acetate in the reactor at beginning of reaction;

Q_{AV} = Mass flow rate of addition of vinyl acetate;

Q_{AB} = Mass flow rate of addition of butyl acrylate;

t = The time of reaction for each sample;

m_0 = initial mass of reagents;

E = Mass of the surfactant + Mass of the initiator

Appendix II :Mechanisms Of Particle Formation In Emulsion Polymerization

HOMOGENEOUS NUCLEATION

Oligomeric free radicals in the aqueous phase propagating until they attain a sufficiently high degree of polymerization to "precipitate", become swollen with monomer and there upon from particles. Charged groups formed from initiation impart colloidal stability.

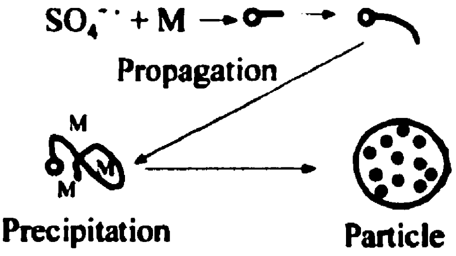

Figure A-1: Homogeneous Nucleation

MICELLAR NUCLEATION:

Initiator radicals generated in the aqueous phase enter the monomer-swollen surfactant micelles, as single radicals, and initiate polymerization to form monomer-swollen polymer particles which grow by propagation reaction. Usually only one out of every 100 – 1000 micelles captures a radical and becomes a polymer particle. Unentered micelles give up their surfactant and monomer molecules to the rowing particles. Particle nucleation ends with the disappearance of the micelles, after which the number of particles generally remains constant. In some cases, however, it may decrease because there is insufficient surfactant to maintain colloidal stability, or it may increase slightly in the later stages of the polymerization due to desorption of surfactant molecules from the surface of the particles causing new particle generation. The monomer droplets, which are relatively large in size (1-10 μm in diameter) serve as reservoirs, feeding monomer to the growing particles by diffusion through the aqueous phase, until they disappear.

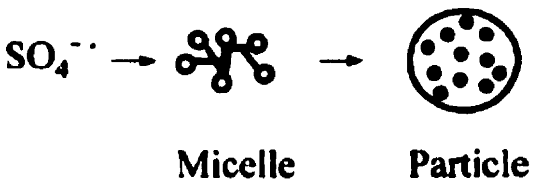

Figure A-2: Micellar nucleation

the time of weighed them. The related mass flow rate at every graduating on the pump were thus determined. The following expression permits to calculate the Reynolds number of the flow:

$$\mathrm{Re} = \frac{\rho_{60} V . d_{it}}{\mu_{60}} \tag{A-5}$$

where

ρ_{60} = 0.97 gr/cm^3 , the density of the emulsion to 60 °C;

μ_{60} = 0.005 gr/cm.s, the viscosity of the emulsion in cm/s;

V = average linear velocity of the emulsion cm/sec

d_{it} = 2.23 cm interior diameter of the tube in Teflon.

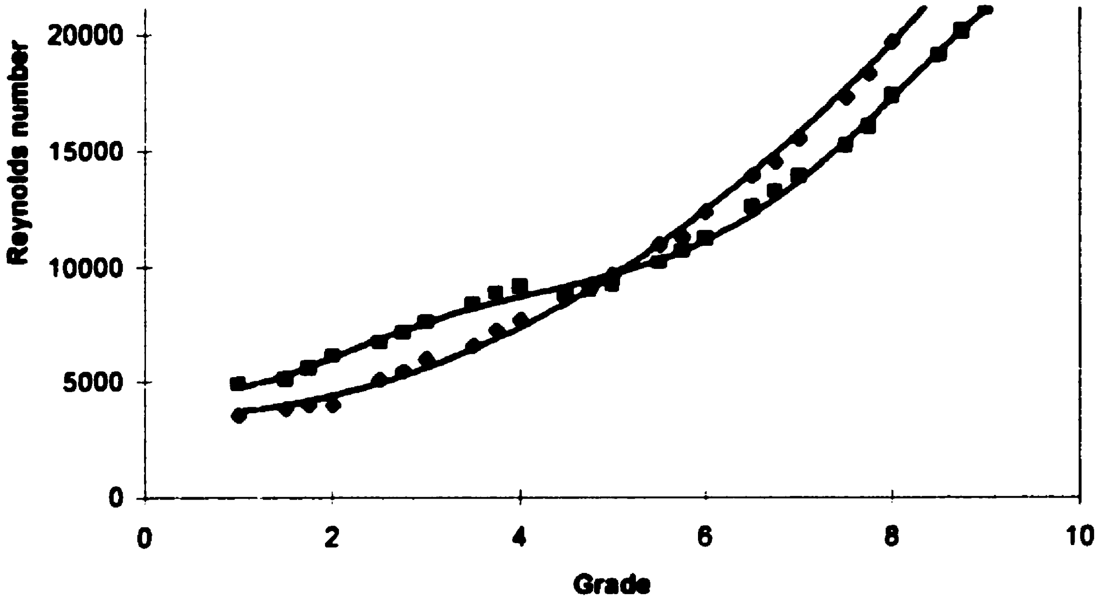

Figure (A-3) : Calibration curve for the tubular reactor without and with static mixer

Appendix IV: Effect of Pump On Emulsion Polymerization

Liquids are moved through pipe, equipment or the ambient atmosphere by pumps. This device increases the mechanical energy of the fluid. The energy increase maybe used to increase the velocity, the pressure and the elevation of the liquid. The most common method of adding energy is by positive displacement or centrifugal action supplied by outside forces. These methods lead to the two major classes of liquid-moving machinery: (1) those applying direct pressure to the fluid and (2) those using torque to generate rotation.

In pumps the density of the fluid does not change appreciably and it is both constant and large. Pressure differences are usually considerable, and heavy construction is needed.

By considering the effect of pumps on the density of liquids, it is clear it has no considerable effect on micelles and particles during the reaction because the pump has no effect on the liquid density and can not have a destructive effect on them by compression.

Appendix V: Calculation Of Copolymer Composition And Reactivity Ratios

A typical vinyl acetate-butyl acrylate copolymer spectrum is given in Figure 3. The copolymer compositions were calculated from the relative intensities by direct integration of the resonances at 5.35 ppm (S_2) and 4.23 ppm (S_1) of the expanded peaks (Figure 4). The peak at 5.35 ppm is the resonance of the CH group in vinyl acetate, and 4.23 pp is the resonance of the $-O-CH_2$ group in butyl acrylate.

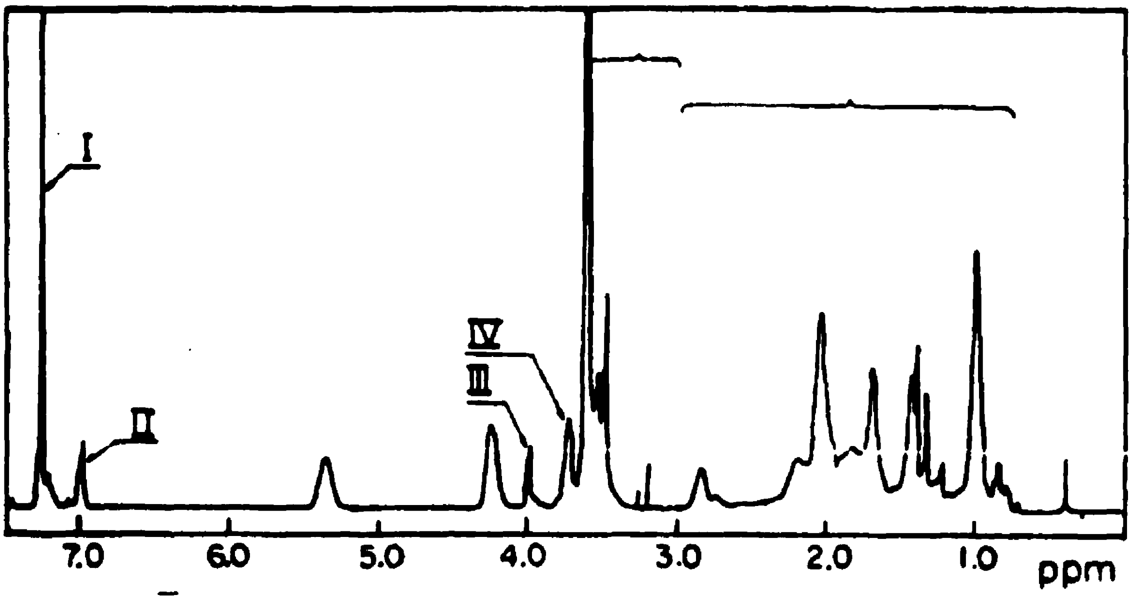

Figure (A-4): ${}^1H$ spectrum of vinyl acetate- Butyl acrylate copolymer

The percentage of vinyl acetate was evaluated using the following equation:

$$\%VAC = \frac{2S_2}{2S_2 + S_1} \times 100$$

Where S_1 and S_2 are the peak areas of the resonance of the peaks at 4.23 and 5.35 ppm, respectively.

For the other peaks of Figure 3 the attributions the main peaks are: Peak I, Residual H of the solvent; Peak II, H aromatic from the polyoxyethylene; Peak III; CH butyl acrylate; Peak IV, CH_2O polyoxylethylene. The group of peaks from 3.0 to 3.6 originates from the various CH_2 of the polyoxyethylene whereas the group of peaks from the lower ppm originates from the copolymer constituents.

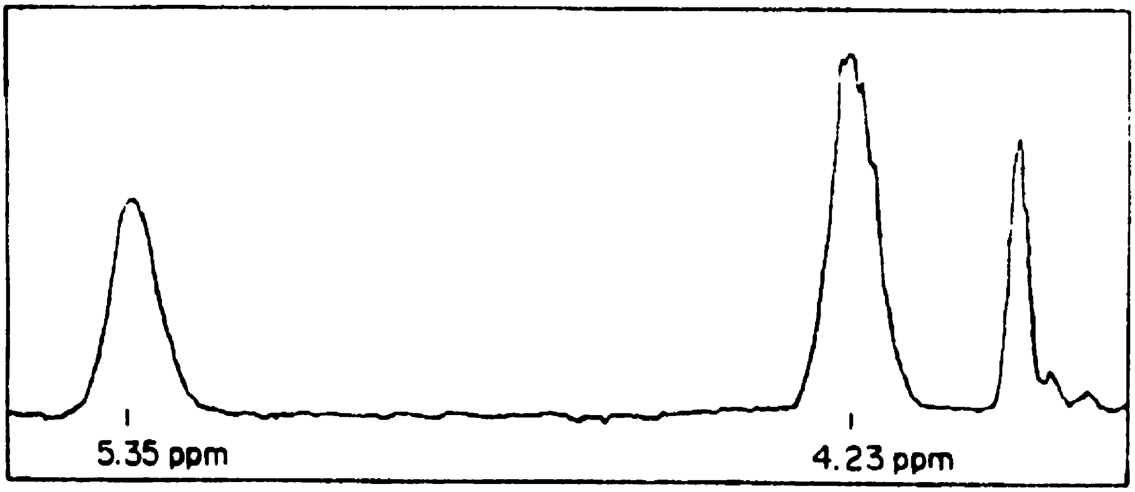

Figure (A-5): Expanded ^{1}H spectrum from 4 to 5.5 ppm of Figure A-4

Bataille and Bourassa (1989) used their method to find the reactivity ratios in low concentrations, but as it is seen, in general curve of copolymer composition (F_1.vs.f_1) it is possible to find $1/r_1$ and $1/r_2$ from this curve. There is no restriction for the concentration of the monomers in feed. The only thing that should be noticed is $1/r_1$ must be found from the shape of curve at f_1=1- in this work because of limitation on data, r_1 is found in this way. After finding r_1, it is put in general equation (4-2) and by knowing F_1, f_1, and r_1 we can find r_2.

NMR data only used to find the composition of copolymer in each sample and it is not limited to low concentrations.

Appendix VI: Protocol For The Utilization Of Vinyl Acetate And Butyl Acrylate

General information on vinyl acetate and butyl acrylate

	vinyl acetate	butyl acrylate
DESCRIPTION	Colorless liquid , very reactive monomer	colorless liquid that can polymerize under influence of light
FORMULA	$C_7H_{12}O_2$	$CH_3COOCHCH_2$
Physical data	Molar mass: 128.2; boiling point: 69 °C in 50 mm; freezing point: -64.6 °C; vapor pressure: 10 mm Hg in 35.5 °C	Molar mass: 86.05; boiling point: 73 °CS; vapor pressure : 100 mm Hg to 21.5 °C

Degree of toxicity

1. SHORT term exposition - materials that are inhaled either absorbed by skin or by the mucous membranes following an exhibition of a length of the second, minutes either hours and for materials that ingested in only one quantity or dose.

	vinyl acetate	butyl acrylate
irritability (effects on skin or on membranes mucous)	weak toxicity	moderate toxicity
INHALATION INGESTION	weak toxicity	moderate toxicity

2. LONG term exposition - applies to the substance that is inhaled, absorbed by skin either ingested of repeated way (days, months or years).

	vinyl acetate	butyl acrylate
irritability (effects on skin or on membranes mucous)	weak toxicity	unknown toxicity
INHALATION INGESTION	unknown toxicity	unknown toxicity

"Weak toxicity" - applies to substances that can produce changes in human body , changes that are reversible and that are going to disappear at the end of the exhibition, with or without medical treatment.

"Moderate toxicity" - applies to substances that can produce reversible or irreversible changeover in the human body. This changeover is not stern enough to threaten life or to produce of important physical affections.

"Unknown toxicity" - applies to substances so that it does not have sufficient of data concerning their toxicity .

Information on the utilization of vinyl acetate and butyl acrylate

Objective of experiences: emulsion copolymerization of vinyl acetate and butyl acrylate

Reactor used: Tubular, of maximal capacity of 3000 ml, installed under a ventilator.

Quantity of monomers used during an experience

- vinyl acetate: 668 - 853 ,added in the tank of emulsion.
- butyl acrylate: 47 - 233 ml, added in the tank of emulsion,

Time of reaction: 2 hours.

Number of experiences per day: 1.

Manipulation of monomers and the final product: under the hood.

Final product:

- Copolymers in emulsion (vinyl acetate-butyl acrylate).
- at the end of each reaction, the emulsion is transferred in an empty bottle that is delivered to the technician responsible for the dangerous product management.