



Characteristics and Evaluations of Monomer for Colloidal Suspension Polymerization

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Abstract

A method is presented for selecting a polyvinyl alcohol as a stabilizing agent for suspension polymerization without carrying out the polymerization reaction. This method is demonstrated for polymerization of water-insoluble and water-soluble monomers. Here the stability of the non-reacting suspension is used to predict the stability of the same system, when it is reacting.

Key Words: Polymerization, colloidal suspension, polyvinyl alcohol, monomers.

Introduction

In suspension polymerization a liquid monomer or a mixture of monomers is dispersed as droplets in another liquid, usually water, by mechanical agitation. To prevent the coalescence of droplets during reaction, suspension agents are added to the system[1].

Polyvinyl alcohols are widely used as protecting agents in suspension polymerization[2]. In this case, the suspension stability is a function of polyvinyl alcohol molecular weight, concentration, degree of hydrolysis and distribution of hydroxyl groups in the macromolecules[3-6]. These factors also influence the interfacial tension between the aqueous phase and monomer or monomers. Usually, increasing the concentration and molecular weight of polyvinyl alcohol leads to smaller droplets.

Water-insoluble and partially water-soluble monomers can be polymerized by suspension polymerization[7]. In the co-polymerization of water-insoluble with partially water-soluble monomers, the droplet monomer concentration is governed by the distribution coefficient between bulk phases of the more soluble water species. This coefficient is, in turn, modified by the presence of the suspension agent.

Polyvinyl alcohol is used as viscosity increasing agent in aqueous systems and nomenclature associated with rheology and the preparation and preservation of preparation containing viscosity-increasing agents [14]. New polymerization techniques for the synthesis of high molecular weight hydrophilic polymers were described [15]. The synthesis of Acrylate adhesives by suspension emulsion and solution polymerization process using various co polymers Styrene and evaluation of there proposed application in transdermal patches[16]. Methyl methacrelate- Sulphopropyl methacrelate co polymer nanoparticles were prepared by free radical polymerization while varying the concentration of initiator and monomer and co polymer composition[17]. From suspension-polymerized poly (methylemethacrelate), - drug released from the system is demonstrated using the Oxprenolol hydrochloride[18]. The possible effects of material related properties like molecular mass and particle related properties like shape, size, specific surface, a model polymer like polyvinyl chloride used in suspension polymerization[8,19].

The selection of a suspension agent for a given reacting system is a time consuming trial and error process. Usually it is necessary to carry out the polymerization reaction to the test of the effectiveness and efficiency of the suspension agent. We developed a procedure for choosing a suitable suspension agent without actually doing the polymerization. In this method the stability of the non-reacting suspension is used to predict the stability of the same suspension when it is reacting. For water insoluble monomers such as styrene, methyl methacrylate, results showed that, if the time for coalescence of about 80% of the monomer phase after it was dispersed in water by agitation for less than 10 min and more than 60 min, the particles in the reacting system coalesce or agglomerate. However, if the time of coalescence of the non-reacting suspension is moderate (10-60 min), suspension polymerization is successfully achieved and individual beads are obtained.

In this work, we showed that, this method could be extended to the suspension polymerization of more water-soluble monomers as well as to the co polymerization of water insoluble and water-soluble monomers.

Materials and Methods

Styrene, Methyl methacrylate and Acrylonitrile were purified by distillation at reduced pressure. Polyvinyl alcohols were obtained from scientific polymer products.

Polyvinyl alcohol solutions were prepared by mixing the appropriate amount of polyvinyl alcohol in double distilled water, stirring at 60 °C until they become transparent. Then solutions were filtered and used freshly.

Interfacial tensions were measured at 60 °C[9]. Stability of the non-reacting suspensions was monitored in a 50-ml cylindrical glass reactor. In the method, 10 ml of monomer, 0.5% hydroquinone and 30 ml of polyvinyl alcohol solution at 60 °C were mixed at constant agitation of 350 rpm for 3 min. Agitation was then stopped and recorded the time for coalescence. This procedure was repeated several times and the average values are reported. Polymerization was carried out in a 1-L glass reactor at 60 °C under nitrogen with constant agitation of 350 rpm. The volume ratio of monomer to aqueous phase was 1:3.

Results

Interfacial tensions between the different monomers used and 0.15 wt% polyvinyl alcohol aqueous solution for polyvinyl alcohol with various molecular weights and degree of hydrolysis are reported in the Table 1.

Table 1: Comparison of interfacial tensions between the different monomers

Polyvinyl alcohol	Styrene	Methyl methacrylate	Acrylonitrile
88-10	6.02	2.94	1.41
88-108	15.04	10.16	5.03
98-78	47.27	32.43	13.18

Interfacial tension decreases as the solubility of the monomer in the aqueous phase increases. Also, interfacial tension diminishes as both molecular weight and degree of hydrolysis of the polyvinyl alcohol decreases.

The stability times of the non reacting suspensions made with the different monomers or their mixtures using several polyvinyl alcohols (0.15 wt %) as suspension agents are shown in Table 2 and Table 3.

Table 2: Stability times for non-reacting suspensions of mixtures of Styrene and Methyl Methacrelate in 0.15 wt% polyvinyl alcohol aqueous solutions

Polyvinyl alcohol	Styrene and Methyl methacrelate (vol. %)				
	0/100	25/75	50/50	75/25	100/0
88-108	29.76	30.80	31.56	35.82	43.75
98-21	0.75	0.80	0.98	1.68	1.48
98-78	0.07	0.09	1.46	2.86	1.54

Table 3: Stability times for non-reacting suspensions of mixtures of Styrene and Acrylonitrile in 0.15 wt% polyvinyl alcohol aqueous solutions

Polyvinyl alcohol	Styrene and Acrylonitrile (vol. %)				
	0/100	25/75	50/50	75/25	100/0
88-10	∞	6.00	11.74	9085	∞
88-25	∞	4.00	9.68	11.05	∞
88-97	4.30	4.40	4.80	13.26	23.45
88-108	11.87	12.20	12.76	16.32	43.75
98-21	0.45	0.05	0.05	0.09	0.11
98-78	0.03	0.03	0.05	0.12	1.62

Analysis of the data demonstrates three types of behavior for the single monomer:

- (i) Polyvinyl alcohol of high degree of hydrolysis (>96%), regardless of their molecular weight, do not stabilize the suspension. The suspension coalesces in less than 02 min after stopping the agitation.

(ii) Polyvinyl alcohols of lower degree of hydrolysis (88%) and low molecular weight (<70,000) yield very stable suspensions. Even after 24 hours, the suspensions have not coalesced appreciably.

(iii) Polyvinyl alcohol of lower degree of hydrolysis (88%) and high molecular weight (>70,000) produce moderately stable suspensions. These suspensions coalesce after 04 to 60 min.

On the other hand, for the suspensions made with mixtures of monomers, only two behaviors are observed:

(a) Polyvinyl alcohols of higher degree of hydrolysis, regardless of their molecular weight, do not stabilize the suspension.

(b) Polyvinyl alcohols of lower degree of hydrolysis, regardless of their molecular weight, yield moderately stable suspensions.

Table 4, 5 and 6 contain a summary of the results on suspension polymerization of Styrene, Methyl methacrelate, Acrylonitrile using polyvinyl alcohol of the three groups identified above.

Table 4: Results of suspension Homo polymerization of Styrene in 0.15wt% polyvinyl alcohol aqueous solution

Polyvinyl alcohol	System Stability	Product
88-10	Unstable – Agglomerated	Lump
88-108	Stable	Beads
98-78	Unstable – Coalesced	Shapeless Bulk

Table 5: Results of suspension Homo polymerization of Methyl methacrelate in 0.15 wt% polyvinyl alcohol aqueous solution

Polyvinyl alcohol	System Stability	Product
88-10	Unstable – Agglomerated	Lump
88-108	Stable	Beads
98-78	Unstable – Coalesced	Shapeless Bulk

Table 6: Results of suspension Homo polymerization of Acrylonitrile in 0.15wt% polyvinyl alcohol aqueous solution

Polyvinyl alcohol	System Stability	Product
88-10	Unstable – Agglomerated	Lump
88-108	Stable	Beads
98-78	Unstable – Coalesced	Shapeless Bulk

Analysis of the data demonstrates three types of behavior can be distinguished:

(i) With polyvinyl alcohol's higher degree of hydrolysis (>96%), the suspended particles coalesce during the reaction. As the solubility of the monomer in the aqueous phase increases, the product goes from a shapeless bulk polymer to polymer lumps. These lumps are formed by very small particles.

(ii) With polyvinyl alcohol's lower degree of hydrolysis (88%) and lower molecular weight polyvinyl alcohol, agglomeration of particles occurs at the final stages of the reaction yielding big polymer lumps. These lumps consist of very tiny particles, which can be easily separated by rubbing them. Particles are easier to disjoin from the lumps in the sequence of Acrylonitrile > Methyl methacrelate > Styrene as in the case of solubility of monomer in water increases.

(iii) With polyvinyl alcohol's lower degree of hydrolysis (88%) and higher molecular weight, reactions are completed without any problem. The products in all cases are isolated beads, which can be easily separated by filtration. Bead size decreases as the aqueous solubility of the monomer increases.

Table 7: Stability of suspension co polymerization of 75/25 by volume Styrene/Methyl methacrelate mixture using 0.15wt% of different polyvinyl alcohol's in water

Polyvinyl alcohol	System Stability	Product
88-10	Stable	Small Lumps
88-96	Stable	Beads
88-108	Stable	Beads
98-21	Unstable – Coalesced	Shapeless Bulk Polymer

Table 8: Stability of suspension co-polymerization of 75/25 by volume Styrene / Acrylo - nitrile mixture using 0.15wt% of different polyvinyl alcohol's in water

Polyvinyl alcohol	System Stability	Product
88-10	Stable	Small Lumps
88-25	Stable	Small Lumps
88-97	Stable	Beads
98-21	Unstable – Coalesced	Shapeless Bulk Polymer
98-78	Unstable – Coalesced	Shapeless Bulk Polymer

When suspension polymerization is carried out with mixtures of monomers, only two types of behavior are observed:

(a) With polyvinyl alcohol's higher degree of hydrolysis (>97%), regardless of molecular weight, particle agglomeration occurs and the final product is a shapeless bulk polymer.

(b) With polyvinyl alcohol's lower degree of hydrolysis (88%), regardless of molecular weight, all the reaction are carried out without agglomeration. In all the cases, polymer beads are obtained which can be isolated by filtration. The beads produced using the lower molecular weight of polyvinyl alcohols are formed by the agglomeration of very fine particles (table 7 and 8).

Discussion and Conclusion

Suspension polymerization is an important industrial process for producing polymers of relatively high purity. Polyvinyl alcohols have become widely used as suspension stabilizers. Their behavior as protective colloids is influenced not only by molecular weight and degree of hydrolysis, but also by stereochemistry, degree of branching and distribution of hydroxyl and acetate groups. The latter factor appears to be particularly important since the industrially used acid hydrolysis process is essentially random making control of block length impossible. Hence, a method for selecting the best polyvinyl alcohol's for a given suspension polymerization, without performing time consuming, trial and error polymerization reactions, is very desirable.

Here we proposed a method for selecting a polyvinyl alcohol for the suspension polymerization of highly water-insoluble monomers. Here we demonstrate that this method can also be used for the suspension polymerization of more water-soluble monomers as well as for the co polymerization of water-insoluble and more water-soluble monomers.

The stability of the non-reacting and reacting suspensions examined here depend on polyvinyl alcohol's molecular weight and degree of hydrolysis. The 88% hydrolyzed polyvinyl alcohol's yield stable non-reacting suspension where as the highly hydrolyzed polyvinyl alcohol's a produced unstable system referring on Table II and III. This difference can be accounted for in terms of the differences in surface activity exhibit by the polyvinyl alcohols as a function of degree of hydrolysis. The highly hydrolyzed polyvinyl alcohols are too hydrophilic and, hence, they do not adsorb strongly enough at monomer-water interfaces to form a coherent film, which will inhibit drop coalescence. By contrast, moderately hydrolyzed polyvinyl alcohols are more surface active and adsorb more strongly at interfaces. This is clear from the values of interfacial tension reported in Table 1.

For single monomers, 88% hydrolyzed, low molecular weight polyvinyl alcohols yield much more stable suspensions than their high molecular weight counterparts. One explanation is that low molecular weight species are more surface active per weight than the higher molecular weight ones (Table 1) and, hence, they are prone to adsorb stronger. Another possibility is that the surface activity of the high molecular weight polyvinyl alcohol's is affected more by the hydroxyl and acetate distributions (because of the randomness of the acid hydrolysis reaction) than that of low molecular weight species. On the other hand, Glass et al[10] showed that low molecular weight (88% OH) polyvinyl alcohols are better stabilizers than the high molecular weight ones. They attributed this to an aging phenomenon, which is related to the formation of a rigid film at the liquid-liquid interface. This aging phenomenon apparently diminishes with increasing molecular weight and degree of hydrolysis.

With mixtures of monomers, however, both low and high molecular weight (88% OH) polyvinyl alcohols give moderately stable dispersion. This result is probably related to the distribution of the more water-soluble monomer among bulk phases and interface. In fact, some molecules of the more water-soluble monomer are likely to stay at the interface, disrupting the adsorbed polyvinyl alcohol's film and altering its rigidity and coherence. Evidently, the low molecular weight polyvinyl alcohol's film is affected more than the high molecular weight one by the intrusion of the small monomeric species.

Regardless of the mechanism of stabilization of the non-reacting suspension by polyvinyl alcohols, the criterion is followed here as well. When the non-reacting suspension is moderately stabilized by the protective colloid, the reacting suspension is stable and yield polymer beads which can be separated by filtration. However, if the stability times of the non-reacting suspension are either too small or too long, the reacting suspension coalesces or flocculated (Table 2 and 7). When the non-reacting suspension is unstable the system coalesce during the reaction yielding shapeless polymer bulk; when the non-reacting suspension is extremely stable, the system agglomerate during reaction yielding polymers lumps consisting of very tiny particles. In most cases, simply rubbing them with the hands can easily separate particles in these lumps.

Another observation is that polymer bead size decreases as the solubility of the monomer in the aqueous phases increases. Evidently, this is the result of the lower interfacial tension exhibited by the more water-soluble monomers. Particle size and particle size distributions are controlled by the ratio of shearing forces to capillary forces[11-12]. In the experiment performed here, agitation rate, propeller type, geometry and viscosity of the aqueous phases were held constant. Hence, particle size and particle size distribution should decrease as the interfacial tension between continuous and disperse phase decreases, in agreement with our results.

In general, our results suggest that high molecular weight (>70,000) and partially hydrolyzed (88%) polyvinyl alcohol are the best suspension agents. Low molecular weight and partially hydrolyzed (88%) polyvinyl alcohol can also be used as suspension agents but bead size and reaction stability are more difficult to control.

In spite of the complexity of the stabilization phenomena, stability time measurements of non-reacting suspension appear to be a valuable tool for selecting the best protective colloid for a given suspension polymerization. This method is useful for selecting not only the type of polyvinyl alcohol but its optimum concentration as well[13]. The results showed that the method is applicable to the suspension Homo and co polymerization of monomers with different aqueous solubility's.

References

- [1] A Dawkins. Comprehensive Polymer Science, Vol. 4, Pergamon Press, New York, **1989**.
- [2] DH Napper. Polymeric Stabilization of Colloidal Dispersions, Academic press, New York, **1983**.
- [3] JMG Lankveld and J Lyklema. *J Colloid Interface Sci*, **1962**, 41,454.
- [4] FH Winslow and M Matreyek. *Ind Chem Eng*, **1951**, 43, 1108.
- [5] HV Hopff; H Lussi and E Hammer. *Makromol Chem*, **1965**, 82, 184.
- [6] E Mendizabal; JR Castellanos-Ortega and JE Puig. *J Colloid Interface Sci*, **1990**, 53, 246.
- [7] M Munzer and E Trommsdorff. High Polymers, Vol.29, John Wiley, New York, **1977**.
- [8] J Brandup and EH Immergut. Polymer Handbook, John Wiley, New York, 1975.
- [9] M Sanchez-Rubio; JR Castellanos-Ortega and JE Puig. *J Chem Ed*, **1991**, 68, 158.
- [10] JE Glass; RD Lundberg and FE Bailey. *J Colloid Interface Sci*, **1970**, 33, 491.
- [11] HV Hopff; H Lussi and P Gerspacher. *Makromol Chem*, **1964**, 81, 24.
- [12] HV Hopff; H Lussi and E Hammer. *Makromol Chem*, **1965**, 82, 184.
- [13] JR Castellanos-Ortega; MStHesis, Universidad de Guadalajara, Guadalajara, Jal, Mexico, **1990**.
- [14] LV Allen. *Int J Pharm Comp*, **1999**, 3(6), 479-486, 501-502.

[15] D Benda; J Snuparek; V Cermak. *J Disp Sci Tech*, **1997**, 18(2), 115-121.

[16] JK Lalla; V R Bapat; VC Malshe. *Ind J Pharm Sci*, **1994**, 56(1), 5-9.

[17] K Langer; C Margburger; A Berthold; J Kreuter; F Stieneker. *Int J Pharm*, **1996**, 137, 67-74.

[18] PI Lee. *J Pharm Sci*, **1993**, 82, 964-967.

[19] AF Rine; D Massuelle; F Kubel; HR Hagemann; E Doelker. *European J of P.Ceutics & Biopharmaceutics*, **1997**, 44(3), 315-322.