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REVIEW PAPER

# Suspension polymerization technique: parameters affecting polymer properties and application in oxidation reactions

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## Abstract

Various heterogeneous polymerization techniques such as suspension, emulsion, dispersion, precipitation and seeded are employed for the synthesis of a wide variety of porous polymer particles. In present review, suspension polymerization technique is highlighted in detail with control of particle size, advantages and its applications. The aim of the review is to understand the basics of suspension polymerization for the synthesis of polystyrene cross-linked with divinylbenzene copolymer. Also, the effect of various synthesis parameters (agitation speed, temperature, initiator, cross-linker and diluent) on particle surface morphology, particle size and distribution, surface area and cross-linking density was reviewed and their application as catalyst support for various oxidation reactions.

**Keywords** Porous polymer · Suspension technique · Agitation · Initiator · Diluent

## Introduction

The wide range of applications of porous polymer particles in various fields such as biotechnology, column packing for gel permeation chromatography and as a catalyst support describe their immense significance to the researchers. Based on the porosity, polymer particles are distinguished as gel and porous. Gel particles are non-porous and low cross-linked, whereas porous polymer particles, especially the ones that are spherical in shape, are highly cross-linked in nature. They have been categorized into three classes, microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm), depending on their pore size (Fig. 1). These differences of porous particles from gel type particles give rise to exceptional important features such as high surface area, ability to uptake various solvents and high brittleness [1–4].

Several methods for the production of polymer particles by various heterogeneous polymerization techniques exist in which the initial monomer and resulting polymer are exist in form of a fine dispersion [5, 6]. The polymerization initiator may/may not be present within the formed polymer during their synthesis and may be soluble in monomer/medium, depending upon the type of polymerization technique. Monomer phase referred as dispersed phase/organic phase and the liquid phase comprising the dispersed phase is referred to as polymerization medium. There are basically five different techniques employed for the synthesis of polymer particles such as suspension, emulsion, dispersion, precipitation and seeded polymerization.

Suspension polymerization technique is usually suitable for the synthesis of large polymer particles (5–1000 μm), while the other processes produce much smaller particles (Fig. 2). In all cases, the application should be kept in mind prior to choosing the method of production [7–17]. In this technique, both initiator and monomer are insoluble in the polymerization medium, while initiator is soluble in the monomer and polymerization takes place in the monomer droplets. The monomer phase is suspended in the medium in the form of small droplets by means of a stirrer and a suitable suspension agent. Examples of polymers synthesized via suspension polymerization include PS, PVC, PAc, PVA, PAAm and water-soluble acrylates [18, 19].

In emulsion polymerization, monomer is insoluble in the polymerization medium which is emulsified by the addition of a surfactant/emulsifier/soap whereas initiator is soluble in the medium and not in the monomer. Under these conditions, the monomer is present in the mixture partly in the

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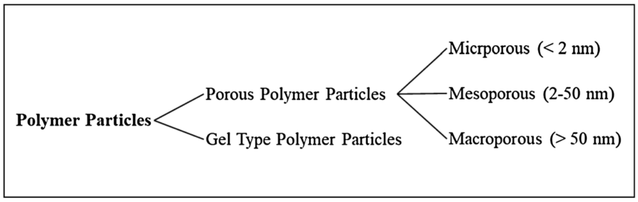


**Fig. 1** Classification of porous polymer particles on the basis of pore size

form of droplets and soap-coated micelles, depending on the nature and concentration of the emulsifier. The ratio of monomer phase to medium is generally 0.1–0.5. Examples of polymers produced by emulsion polymerization include PS, PMMA and PAAm, etc. [20–25].

In dispersion polymerization, polymerization is originated in homogeneous solution as both monomer and initiator are soluble in the polymerization medium. Depending on the solvency of the solution, phase separation occurs at an early stage, which leads to formation of primary particles, thus swollen by the polymerization medium. Therefore, polymerization reaction proceeds largely within the distinct droplets, leading to the formation of spherical shaped polymer particles. Examples of polymers formed via dispersion polymerization include PS, PMMA, etc. [26–30].

Precipitation polymerization is a non-homogeneous technique that starts with homogeneous system where both initiator and monomer are completely soluble but formed polymer is insoluble and therefore precipitates. Examples of polymers synthesized through precipitation polymerization include TFE, ACN, etc. [31–36].

In seeded polymerization technique, monodisperse seed particles formed by suspension/emulsion polymerization are treated first with a suitable oligomer, and then with monomer and an oil-soluble initiator. This mixture is completely absorbed by the particles and successive polymerization leads to the formation of larger monodisperse particles. This is an excellent technique where monodisperse particles can be grown from few micrometers to hundreds of micrometer by consecutive monomer swelling. Examples of polymers produced by seeded polymerization include PS, PMMA, etc. [37–39].

Seeded polymerization method is costly and complex to be carried out, while dispersion and precipitation techniques are comparatively easy and efficient for the synthesis of monodisperse polymer particles with one drawback that organic solvent is unfriendly to the environment. The difference between suspension and emulsion polymerization lies in their particle size. Emulsion technique contains particles less than 1 μm in size whereas suspension contains greater than 1 μm. Table 1 shows the comparison of different polymerization techniques on the basis of different parameters. Hence, one should consider several parameters (size, size dispersion, pore size, porosity, shape, and cost) before choosing the polymerization method for the synthesis of polymer particles [40, 41].

Based on the literature review, suspension polymerization method is simple to operate and easy to perform. However, its application is limited due to large particle size, size distribution and high value of coefficient of variation (CV; ratio of standard deviation to the mean of particle size). Higher the value of CV, higher the level of dispersion in particle size, which is usually not required. Although suspension polymerization method is not a new technology, but, if small size monodisperse-porous polymer particles could be produced from this technique by altering various synthesis parameters (e.g. amount and type of initiator, crosslinker and diluent, agitation speed and temperature), then it can be a cost-effective technique which has the ability to scale up in industry [9, 42–52]. Thus, the current section comprises the literature survey of suspension polymerization method in brief.

## History of suspension polymerization

This technique was first developed by Hoffman and Delbruch in 1909 [53]. Around 20–30 years later, Svec

**Fig. 2** Schematic flow diagram of particle size range of heterogeneous polymerization processes

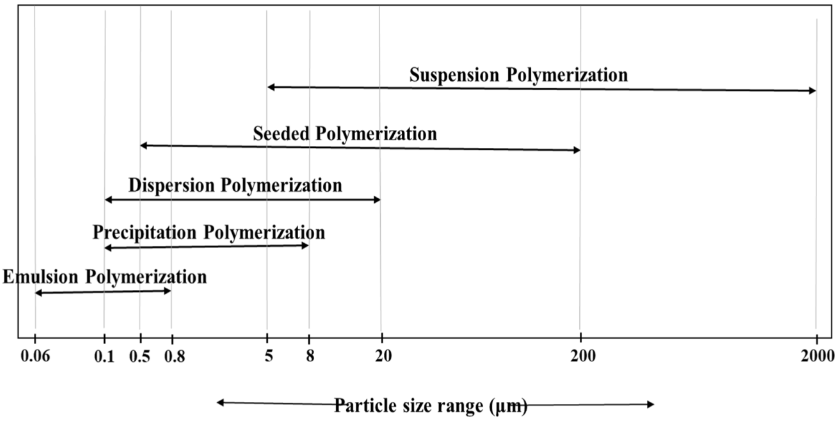


**Table 1** Comparison of different polymerization techniques on the basis of various parameters

| Techniques | Discovery | Particle size (μm) | Solubility in medium | Easiness/ Cost | CV | Particle size distribution | Applications | Examples |
|---|---|---|---|---|---|---|---|---|
| Suspension | 1920 | 5–2000 | Monomer and initiator both are insoluble | Easy and cheap | Very high | Polydisperse | porous polymer | PS, PVC, PVA, etc. |
| Emulsion | 1920 | 0.06–0.8 | The monomer is insoluble and the initiator is soluble | Easy but can be costly | Very high | Polydisperse | porous polymer | PS, PMMA, PAAm,,etc. |
| Dispersion | 1970 | 0.1–20 | Monomer and initiator both are soluble | Easy and cheap | 2–3% | Monodisperse | nonporous and cross-linked polymer | PS, PMMA, etc. |
| Precipitation | 1990 | 0.1–8 | Monomer and initiator both are soluble | Easy but can be costly | 2–3% | Monodisperse | Highly porous and cross-linked polymer | TFE, ACN, etc. |
| Seeded | 1980 | 0.5–200 | Monomer and initiator both are soluble | Cheap but can be time-consuming | 2–3% | Monodisperse | Uniform porous polymer particles | PS, PMMA, etc. |

et al. studied the synthesis of porous polymer particles using free radical suspension polymerization [54–61]. The internal particle morphology in suspension polymerization was first predicted by A. H. Alexopoulos and coworkers [62] and L. Tan have reviewed the synthesis of hyper cross-linked porous polymers [63]. Although suspension polymerization has been broadly studied over more than 50 years, but the present situation is that its understanding is still limited and lack of its application at the industrial level. Also, effect of various parameters on polymer synthesized via suspension polymerization are not considered in detail in previous reviews, therefore, the aim of the present review is to study the effect of various synthesis parameters for the production of PS-co-DVB copolymers.

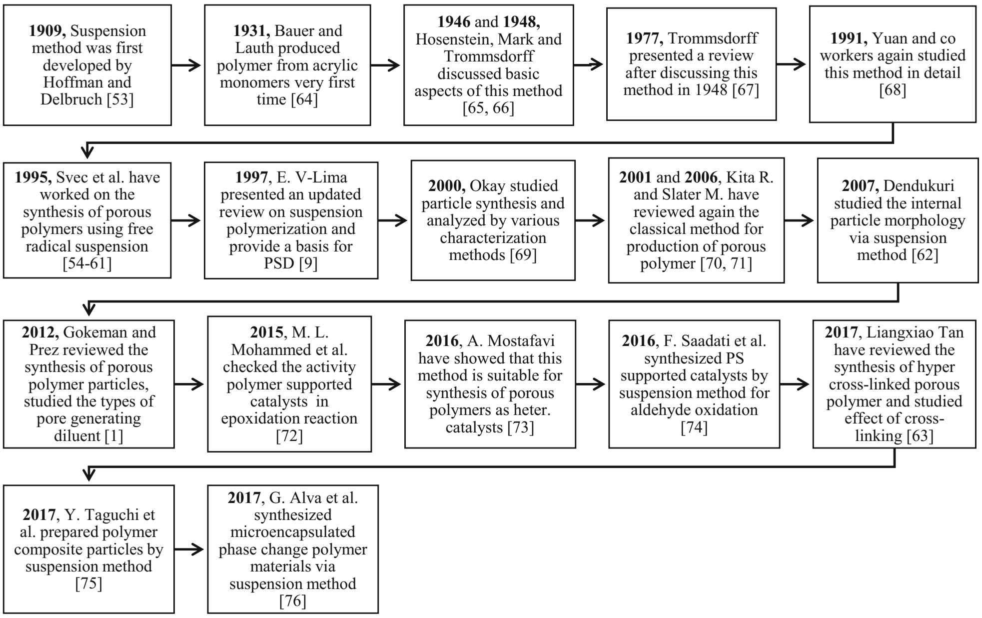
Figure 3 shows the schematic flow diagram for the development of suspension polymerization technique.

## Suspension polymerization

### Outline

Suspension means the solid/liquid dispersion. It starts with liquid/liquid dispersion and ends with solid/liquid dispersion. The least sophisticated heterogeneous polymerization technique starts with the formation of organic and aqueous phases separately. Organic phase to aqueous phase volume ratio usually varies from 0.1 to 0.5 or even more. The organic phase is prepared by the addition of monomer, initiator, crosslinker molecules and diluents, on the other hand, surfactant and stabilizer are dissolved in distilled water to make aqueous phase [77–80]. Monomer droplets are dispersed in an aqueous phase with the addition of surfactant molecules (sodium dodecyl sulfate/sodium sulfate) and stabilizer (methylcellulose/PVA/gelatin) to prevent coalescence and breakage during

**Fig. 3** Schematic flow diagram of development of suspension polymerization method



**1909,** Suspension method was first developed by Hoffman and Delbruch [53]

**1931,** Bauer and Lauth produced polymer from acrylic monomers very first time [64]

**1946** and **1948,** Hosenstein, Mark and Trommsdorff discussed basic aspects of this method [65, 66]

**1977,** Trommsdorff presented a review after discussing this method in 1948 [67]

**1991,** Yuan and co workers again studied this method in detail [68]

**1995,** Svec et al. have worked on the synthesis of porous polymers using free radical suspension [54-61]

**1997**, E. V-Lima presented an updated review on suspension polymerization and provide a basis for PSD [9]

**2000,** Okay studied particle synthesis and analyzed by various characterization methods [69]

**2001** and **2006,** Kita R. and Slater M. have reviewed again the classical method for production of porous polymer [70, 71]

**2007,** Dendukuri studied the internal particle morphology via suspension method [62]

**2012,** Gokeman and Prez reviewed the synthesis of porous polymer particles, studied the types of pore generating diluent [1]

**2015,** M. L. Mohammed et al. checked the activity polymer supported catalysts in epoxidation reaction [72]

**2016,** A. Mostafavi have showed that this method is suitable for synthesis of porous polymers as heter. catalysts [73]

**2016,** F. Saadati et al. synthesized PS supported catalysts by suspension method for aldehyde oxidation [74]

**2017,** Liangxiao Tan have reviewed the synthesis of hyper cross-linked porous polymer and studied effect of cross-linking [63]

**2017,** Y. Taguchi et al. prepared polymer composite particles by suspension method [75]

**2017,** G. Alva et al. synthesized microencapsulated phase change polymer materials via suspension method [76] polymerization. Also, monomer soluble initiator (free radical) is added for both initiation and chain growth mechanism within the monomer droplets, however monomer and initiator, both are insoluble in the medium. The initiation and propagation mechanism occurs inside the monomer droplets. The product is collected by conventional filtration and washed to eliminate stabilizer and other contaminants [81–83].

The terms pearl and bead polymerization are also used for suspension polymerization when the porosity of polymer particles is not desired. Suspension polymerization may be classified into two types on the basis of polymer solubility in the monomer i.e. suspension bead and suspension powder polymerization (Fig. 4). An example of PS-co-DVB copolymer synthesis is presented to understand the synthesis mechanism of suspension polymerization, followed by the study of effect of various synthesis parameters.

### Synthesis of PS-co-DVB copolymer

PS is one of the most widely used polymer due of its salient features such as low cost, readily availability, chemical inertness and easy functionalization. Different types of cross-linker agents are incorporated into the PS resin matrix (PS-co-DVB) to improve the polymer rigidity, cross-linking density and surface area, such as DVB, EGDMA and TEGDA, the most common being DVB [10, 84].

For use of PS-co-DVB as catalytic support in different chemical reactions, it is desirable that it should have a small particle size, uniform size distribution, high porosity, cross-linked, high surface area, high activity and selectivity, high thermal, mechanical and chemical stability [85–89]. To achieve these properties, various synthesis parameters play a major role and by altering their amount and type, one can synthesize the desired polymer. Using organic polymer is highly advantageous as one can easily alter polymer properties during its synthesis, according to the desired application. From all the synthesis parameters available, some physicochemical parameters (stirring speed, temperature, monomer, initiator, cross-linker and diluent) are discussed briefly (Fig. 5).

Effect of agitation speed and temperature is well established in the literature. Particle size and agitation speed both are inversely proportional to each other. It is reported in the literature that agitation speed should have a range of 200–800 rpm; below and above this value, there will be rigorous conditions with rough particle surface and non-uniform distribution [90].

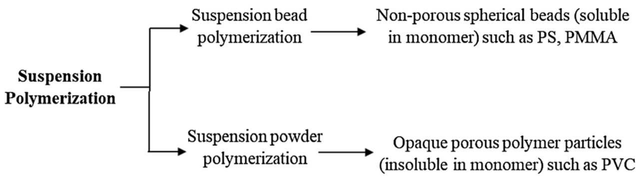


**Fig. 4** Type of suspension polymerization methods

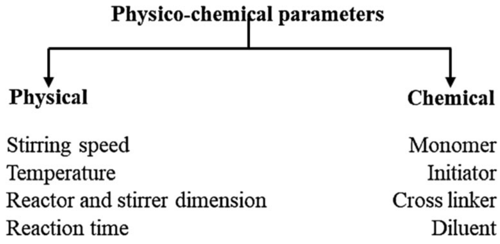


**Fig. 5** Parameters affecting polymer properties during synthesis

Further, higher the polymerization temperature smaller will be the polymer particle size. Also, there is a limit to the temperature range for polymerization (40-90 °C) [91–94]. Hence, agitation speed and temperature are major factors controlling the polymer particle size during their synthesis. Next, polymerization reaction time has no significant effect on polymer particle size and size distribution. However, type of monomer (hydrophilic/hydrophobic) affect the polymerization reaction mechanism. Selection of monomer depends upon the type of polymerization technique used, reaction medium and type of comonomer. During suspension polymerization, styrene and divinylbenzene (hydrophobic) and distilled water (reaction medium; polar in nature) are used, because hydrophobic monomers have high level of swelling and less retention for polar solvents. On the other hand, initiator, cross-linker and diluent have major effect on polymer particle properties, which are described in detail below.

## Effect of initiator amount

Initiator is one of the elementary components used in the heterogeneous polymerization. Its nature and concentration decide the topochemistry of the initiation reaction [95]. The effects of the type of initiator on the kinetics of heterogeneous polymerization, on the stability of the reaction methods and on the size and size distribution of polymer particles are reported in the literature [52]. AIBN and BPO are the most widely used initiators in case of PS-co-DVB copolymer [48].

Kiatkamjornwong et al. [44] have reported the effect of initiator amount on polymer properties by changing the amount from 0.1 to 2.0 wt.% of the monomer concentration. The results shown that the conversion increased with initiator amount as more free radicals formed in the initiation period. At low initiator concentration, holes were generated on the particle surface because of crosslinking reaction; spherical particles with fusion were appeared at higher initiator concentration. Therefore, initiation rate affects the polymerization rate. Although, droplet coalescence can occur when the monomer droplets are not stabilized, which might show the insufficient amount of stabilizer in the monomer droplets.

Ober et al. [45] showed the effect of initiator amount at two different temperatures (68 °C and 75 °C) by changing the initiator amount from 1.0 to 2.0 g. In the first case, it was shown that the rate of free radical formation enhanced when the initiator amount increased, which leads to faster initial monomer consumption but also produced larger particle of lower molecular weight**.** At 75 °C, lower amount of initiator (0.55 g) was required to produce particles with smaller size, narrow size distribution and much higher molecular weight than at 68 °C.

The results revealed that at lower initiator amount (0.1 wt.%), particles produced with a rough surface and broader size distribution, however, at higher concentration (more than 2.0 wt.%), particles with smooth surface were obtained. It was shown that lower initiator amount could produce higher molecular weight polymer and vice versa. Also, the initiator amount was reduced when polymerization took place at higher temperature. Therefore, polymer particle size may increase or decrease on increasing the initiator amount and type of monomer used. Therefore, only a particular set of reaction conditions gave monodispersity with smaller size and with more or less initiator produced particles with wider distributions and the optimum particle uniformity may be obtained at some value in between lower and higher ones.

## Effect of cross-linker amount

Cross-linking agents are used for the cross-linking among the monomer units, which affect the polymer properties. The effect of the type and amount of cross-linker agents on heterogeneous polymerization, particle surface morphology, size and size distribution and surface area, were examined by various researchers. Choice of type of the cross-linker agent depends upon the kind of monomer and polymerization technique employed. DVB, EGDMA and TEGDA are most widely used cross-linkers in case of PS-co-DVB copolymer [44].

Hulubei et al. [52] presented the effect of the cross-linker agent on polymer attributes by analyzing that porous structure starts to form after a critical value of cross-linker. The cross-linked polymers exhibited various morphologies depending on the diluent and cross-linker amount in the reaction mixture. As cross-linker amount increased in the reaction system, it leads to the creation of more rigid structures, with an increase of the pores and decrease of their size. At the same time, the cross-linker amount had a major effect on the surface area, which increases on increasing cross-linker content, and particle size, decreases with cross-linker content.

Mane et al. [96] reviewed the changes in polymer characteristics with cross-linking density. Higher cross-linking density improves the surface area and pore volume whereas decreases the pore size. Further, cross-linker increased thermostability, glass transition temperature and improved thermal properties. Low cross-linked polymers have the tendency of greater swelling whereas high surface area and pore volume encouraged the polymer swelling. Cross-linking agents offer insolubility, rigidity and stiffness to the polymer which proposed potential uses in various applications.

Therefore it was observed that higher the amount of cross-linker agent, greater the cross-linking density, higher the surface area, higher rigidity, improved thermal properties, decreased pore and particle size. Usually, during the experiments, the value of cross-linker agents varies from 0.1 to 40.0 wt.% of the monomer amount. At lower amount, polymer particles were produced polydispersed and fused because of insufficient crosslinking sites to maintain polymer particle sphericity. As content increased, particles produced were harder and tougher with smooth surface [97]. Thus, an optimum value will get after performing a number of experimental runs at various reaction conditions.

## Effect of diluent amount and type

The polymer may be formed porous by the insertion of inert diluent (toluene, THF, n-hexane, n-heptane and MEK) in the monomer phase. The diluent is also called porogen i.e. a pore generating solvent, which attributes to polymer properties. The thermodynamic affinity of the diluent with the polymer is predicted by the solubility parameter and therefore, thermodynamic affinity finally controls the porous structure formation for polymer particles. The solubility parameter difference between monomer and diluent decides that which diluent should be considered a good or bad for a polymer. A diluent is considered a good solvent when this difference is zero or smaller than unity and a poor solvent when it is greater than unity. Both good and bad solvents have different extent of phase separation due to their different solvency which influences the polymer properties. Usually, it is said that higher the diluent solvating power, lower the porosity and higher the surface area [98–102].

Based on the literature survey, Toluene, THF and cyclohexane are considered good, among which, toluene gives the best result in case of PS-co-DVB copolymer (Table 2). Apart from the diluent type, the diluent amount is also one of the most significant factors which affect the polymer characteristics. The diluent amount with respect to monomer (monomer/diluent (*v*/v)) may vary from 1:1 to 1:6 or even more.

Mane et al. [103] redefined the effect of diluent on polymer properties and showed that the selection of a right porogen or a porogen pair (a pair of good and bad solvent) is an essential step before the synthesis of polymer particles because an improper porogen selection may give the low porosity polymer. The solvating porogen suggests a greater surface area (generation of micro/mesopores) although non-solvating porogen is able to generate a polymer with smaller surface area (generation of meso/macropores). Experiments were also performed to study the effect of the diluent amount by varying the monomer/

**Table 2** Solubility parameter difference of diluents with PS polymer

| Type of diluents | Solubility parameter difference |
|---|---|
| Toluene | 0.65 |
| THF | 0.76 |
| Cyclohexane | 0.90 |
| Acetone | 1.00 |
| Heptane | 1.10 |
| n-Hexane | 1.15 |
| n-Butane | 1.26 |
| Pentane | 1.32 |
| Ethanol | 1.49 |
| Methanol | 1.79 |
| Water | 3.24 |

diluent ratio from 1:1 to 1:4. After analysis of the results, it was revealed that particle size distribution was uniform in case of 1:1 and 1:2, while in other cases, non-uniform particle distribution was achieved. This type of performance may be due to the emulsion formation at the higher diluent amount, which did not allow polymer formation, also, there was coalescence, fusion and non-uniformity in size distribution.

Hao et al. [104] reported the effect of diluent content on polymer porosity and other properties. They have varied the diluent concentration from 0.66 to 7.0 (diluent/monomer (*w/*w)) and obtained the monodispersed polymer particles at 1.0 diluent/monomer content. With the increase of this value, the particle size distribution changed to polydispersity, especially above 3.0 diluent/monomer ratio.

Therefore literature results showed that good solvent has the smaller and greater miscibility in aqueous and organic phase, respectively, which allow the later phase separation between aqueous and organic phase, whereas bad solvent allows earlier phase separation. Thus, miscibility is not favored in case of bad diluent and it is separated out in an early stage. Also, the amount of diluent is very significant to synthesize the desired polymer, as optimal value achieved at around 1:1 monomer/diluent weight ratio, because at higher ratio emulsion formation were observed.

After studying the effect of various parameters during suspension polymerization, next section describes the control of particle size in brief. The major aim of the suspension polymerization technique is the formation of small size uniform dispersion of monomer droplets in the continuous phase with controlled coalescence of droplets. Droplets change from a low viscosity liquid to a sticky polymer-monomer mixture of increasing internal viscosity during the polymerization reaction and at last converted into porous polymer particles. Initially, the viscosity of monomer-polymer phase is low so breakage occurs easily, therefore breakage play an important role in controlling the droplet size at this time. But breakage becomes difficult as polymerization continues and viscosity increases. Now there is coalescence along with breakage which leads to an increment in droplet size because high viscosity limits the breakage of particles. After some time and above certain monomer conversion, there are no coalescence and polymer particles become hard [8]. Size distribution of initial monomer droplets and hence polymer particles depend upon the balance between break-up and coalescence of droplets, which is then controlled by the type and speed of the agitator, monomer and stabilizer used [105–109].

| Advantages | Disadvantages |
|---|---|
| • Easy removal of heat and control of temperature | • Wastewater problems |
| • Polymer product with low impurity levels | • Lower productivity for the same reactor capacity |
| • Low separation cost | • Polymer build up on the reactor wall |
| • Low dispersion viscosity | • Difficulty in achieving higher conversion |
| • Final product in particle form | • longer duration is required for higher conversion |
| • Average molecular weight of 60,000 is possible | |
| • Economical since water is used as heat transfer medium | |
| • Isolation of product is easy due beads formation | |

After concluding the revision of basic aspects of suspension method, effect of numerous synthesis parameters for PS-co-DVB copolymer particles, followed by advantages and disadvantages, next section of the article refer to the application of PS-co-DVB copolymer as catalyst support in various oxidation reactions in past 10 years.

## Applications of PS supported catalysts in oxidation reactions

In industrial chemistry, catalytic oxidation reactions play an important role for the synthesis of numerous useful chemicals and intermediates (hydrocarbons, diols, alcohols and carbonyl). These reactions are carried out in the presence of various environment-friendly oxidants such as $H_2O_2$, TBHP and $O_2$ [110–112]. Thus, great advances have been made in last few years for the development of new catalysts and efficient processes for several oxidation reactions.

Many catalytic supports such as silica, alumina, porous polymers, activated carbon and zeolites have been used for oxidation reactions [113, 114]. Organic polymers have been extensively explored as catalytic support during the last one decade as they are inert and can be easily functionalized. PS-co-DVB copolymer has shown outstanding activity in

**Table 3** Applications of PS supported catalysts synthesized by suspension method in oxidation reactions

| PS supported catalysts | Applications | Oxidant | Reaction conditions | Remarks | References |
|---|---|---|---|---|---|
| *N*, *N*-bis (o-hydroxy acetophenone) hydrazine/PS-$Cl_2$ | Oxidation of phenol and cyclohexene | $H_2O_2$ | Temp = 70 °C<br>Atmospheric pressure<br>Reaction time = 1400 min | Schiff base complexes of Cu (II) and Zn (II) have shown lower catalytic activity than Fe (III) ions,therefore selectivity for epoxy cyclohexane is higher in case of Fe (III) ions and also showed dependency on the type of polymer support | [127] |
| Ru(salophen)/PS-$Cl_2$ | Oxidation of cyclooctene | $NaIO_4$ | Room temperature<br>Atmospheric pressure<br>Reaction time = 2400 min | [Ru(salophen)PS-$Cl_2$] was used as a highly capable catalyst for alkenes oxidation with 34–100% conversion of the alkenes in presence of sodium periodate oxidant | [128] |
| Poly(amidoamine) dendrimer –Mn(II)/PS | Oxidation of secondary alcohols | Urea–hydrogen peroxide adduct | Temp = 100 °C<br>Atmospheric pressure<br>Reaction time = 180 min | Under mild reaction conditions Mn (II) complexes were reported as efficient catalysts for the oxidation of secondary alcohols in presence of green oxidant (urea–hydrogen peroxide adduct) as they offer new opportunities for the growth of novel supported catalysts | [129] |
| PS–DA–M/PS-$Cl_2$ (M = $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$) | Allylic oxidation of cyclohexene | $O_2$ | Temp = 70 °C<br>Atmospheric pressure<br>Reaction time = 600 min | PS–DA–Cu showed maximum catalytic activity (52%) among all metal complexes. These complexes were found to be very active and selective for the oxidation of cyclohexene with cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 2-cyclohexene-1-hydroperoxide products | [130] |
| $Mo(CO)_6$/PS-DVB | Oxidation of alkenes | TBHP | Room temperature<br>Atmospheric pressure<br>Reaction time = 150 min | Mo supported catalyst was used for epoxidation of variety of alkenes with no loss of activity even after ten times of recycling. Cyclooctene was oxidized with 100% selectivity, while 69–90% selectivity was obtained for cyclohexene with conversion of 80–95% | [131] |
| Cu (II)-Mn(II)/PS | Oxidation of styrene | TBHP and $O_2$ | Temp = 30–80 °C<br>Atmospheric pressure<br>Reaction time = 3600 min | TBHP oxidant at 70 °C and 25 mg catalyst with styrene to TBHP mole ratio of 1:3, showed maximum selectivity to styrene oxide (78.3%) in comparison to $O_2$. | [86] |
| Mo/PS | Oxidation of 4-vinyl-1-cyclohexene | TBHP | Temp = 60–80 °C<br>Atmospheric pressure<br>Reaction time = 240 min | In comparison with experiments carried out in a classical batch reactor, reaction in continuous reactor has shown advantages of fast heat and mass transfer, flexibility of scaling-up reactions and remarkable catalyst stability | [132] |
| Pd-NPs/Carboranyl-PS | Oxidation of glycerol | $O_2$ | Room temperature<br>Atmospheric pressure<br>Reaction time = 1440 min | The well-dispersed, polymer-supported palladium nanoparticle composite was found to be an efficient catalyst for glycerol oxidation reaction | [133] |
| AuNPs/PS-$NH_2$ | Oxidation of benzyl alcohol | $O_2$ | Temp = 50 °C<br>Atmospheric pressure<br>Reaction time = 1440 min | This novel composite exhibited high activity with less selectivity for the benzaldehyde product and also applicable to the oxidation of 1-phenyl ethanol, as a secondary alcohol, to aceto phenone in high yield | [125] |

**Table 3** (continued)

| PS supported catalysts | Applications | Oxidant | Reaction conditions | Remarks | References |
|---|---|---|---|---|---|
| Au-NPs/PS | Oxidation of 1,4 dioxane | TBHP, $O_2$ and $H_2O_2$ | Temp = 80 °C<br>Atmospheric pressure<br>Reaction time = 1440 min | Gold nanoparticles supported on PS were found to be highly active for liquid phase oxidation of 1, 4 dioxane using $O_2$ at low temperature, also, pure $O_2$ in contact with organic liquids is potentially hazardous due to combustible nature of the reaction mixture | [134] |
| [Fe(III)Azo]/CMPS | Oxidative bromination of organic compounds | $H_2O_2$ | Room temperature<br>Atmospheric pressure<br>Reaction time = 360 min | The catalyst was stable under the reaction conditions, also, reusability of this catalyst is high (five times) without significant decrease in its activity | [135] |

oxidation of various hydrocarbons and alcohols to aldehydes, ketones, epoxides and acids. Very first time in 1980, D. C. Sherrington has evolved that polymers can be used as catalysts as well as supports in chemical reactions [115]. In respect to polymeric supports, it was reported that about 65% of the reviewed catalytic systems are based on PS support and 15% are derived from PMMA and PEG and 20% are based on other systems [116–119]. The support that Merrifield used for his initial work (1984) in solid-phase peptide synthesis was based on 2% DVB cross-linked PS [120].

Various transition metals (Ru, Pt, Pd, Au and Ag) have shown high activity for liquid phase oxidation of alcohols [121–123]. For better catalytic activity, higher surface area, stability and dispersion of metal particles is required. Among various organic mesoporous materials, PS-co-DVB has shown high catalytic performance for alcohol oxidation [124]. Kaboudin et al. [125] reported the synthesis of AuNPs/PS-$NH_2$ catalyst for selective oxidation of benzyl alcohol at mild reaction conditions (80 °C) by using air as an oxidant. Saadati et al. [74] investigated the performance of Cu (II) Schiff base complex supported on PS-co-DVB for catalytic oxidation of aldehydes using TBHP as oxidant. Recently, Wang et al. [126] reported the Fe-Co/S-PS supported catalysts for the oxidation of cyclic ketones using $H_2O_2$ as an oxidant. Table 3 summarizes the review of PS-co-DVB copolymer supported catalysts, synthesized by the suspension method, in the oxidation of alkenes, alkanes, alcohols, phenols, aldehydes and ethers.

## Conclusions

- A broad range of heterogeneous polymerization techniques such as suspension, emulsion, dispersion, precipitation and seeded polymerizations were discussed concisely. However, suspension polymerization technique is described in detail for understanding its fundamentals in a very simple way
- Synthesis of polystyrene polymer was reviewed through suspension polymerization method and effect of various synthesis parameters was summarized during the copolymerization of PS-co-DVB
- Porous PS-co-DVB copolymer has shown significant growth as catalyst support for various reactions due to their bulky pore diameter and uniform particle size distribution with a smooth surface
- Lastly, PS-co-DVB copolymer supported catalysts have been discussed for various oxidation reactions and all the catalysts have shown high activity and selectivity for the desired product

**Abbreviations** *PS,* Polystyrene; *DVB,* Divinyl Benzene; *AIBN,* Azobiz isobutyl nitrile; *THF,* Tetrahydrofuran; *PMMA,* Polymethyl methacrylate; *PEG,* Polyethylene glycol; *BPO,* Benzoyl peroxide; *EGDMA,* Ethylene glycol monomethyl ether; *TEGDA,* Tetraethyleneglycol diacrylate; *PVC,* Polyvinylchloride; *PVA,* Polyvinyl acetate; *PAAm,* Polyacrylamide; *TFE,* Tetrafluoro-ethylene; *ACN,* acrylonitrile; *PE,* Polyethylene; *PAc,* Polyacrylates

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