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Dispersion Copolymerization of Styrene with Vinylbenzyl-Terminated Polyoxyethylene Macromonomer

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Summary: Macromonomer with styrenic polymerizable group was synthetized by anionic polymerization of ethylene oxide initiated by potassium vinylbenzyl alcoholate. p-Vinylbenzyl-terminated polyoxyethylene macromonomer (PEO-VB) was then copolymerised with styrene in water/alcohol continuous phase. The resulting polymer is chiefly non soluble in that medium, and the final state is polymer particles in the range 500-1000 nm in diameter stabilized by a macromonomer-rich copolymer. The conversion time curve consists of three regions. The length of nucleation period was inversely proportional to the volume ratio ethanol/water (E/W). The dependence of the polymerization rate (R_p) vs. conversion is described by a curve with two-rate intervals. The rate of polymerization increased with increasing PEO-VB and initiator AIBN concentration but was nearly independent of the volume ratio E/W. The particle number slightly increased with increasing PEO-VB and AIBN concentration. The molecular weight of graft copolymer increased with increasing the volume fraction of water, PEO-VB and AIBN concentration.

Introduction

Amphiphilic graft copolymers are conventionally prepared in solution or disperse media by the radical copolymerization of a hydrophilic (macro)monomer and hydrophobic comonomer and vice versa. These materials are of great interest because of their surface-active properties. They are widely used as an alternative method for the preparation of monodisperse polymer particles [1)]. The graft copolymers prepared from styrene and PEO macromonomer were found to form micellar aggregates in polar media [2)]. In the dispersion copolymerisation of amphiphilic PEO macromonomer, the kinetics of solution polymerization governs the initial stage of polymerisation and the formation of graft copolymers. At this stage of copolymerization the formation of homopolymers of macromononer and comonomer is strongly reduced. The initial stage is accompanied with the transfer of the reaction loci from the solution to the compartmentalized reaction system (polymer particles). Particles are formed by precipitation of growing polymer chains and subsequently stabilized. The critical chain length for precipitation is largely controlled by the nature of the continuous reaction media. A good solvent stabilizes the growing polymer particles in solution. The reaction

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medium is selected in such a way that it acts as a precipitant for the polymer formed and a good solvent for the monomer and stabilizer. The reaction kinetics is a combination of three possible reaction loci: the continuous phase, the interfacial layer and hydrophobic particle core. The kinetic and colloidal parameters of the dispersion copolymerisation are known to be effected by the nature and concentration of (macro)monomers, initiator and additives, the reaction medium and temperature.

The earlier studies have been concentrated mainly on the kinetics of dispersion (co)polymerisation of conventional monomers such styrene, methyl methacrylate, etc [3-6]. Much less effort was devoted to the dispersion (co)polymerisation of styrene where the graft copolymer (stabilizer) is formed in situ. In the previous paper [7] we have prepared PEO macromonomer containing styrenic polymerizable group and then it was used in emulsion copolymerisation with styrene. The copolymerisation was very fast and the particle diameter of polymer latexes was less than 75 nm.

The major purpose of this work is to study the kinetics of dispersion copolymerisation of p-vinylbenzyl-terminated polyoxyethylene (PEO-VB) macromonomer and styrene. This comprises the effect of macromonomer concentration and the nature of continuous phase on the kinetic and colloidal parameters of the dispersion copolymerisation of PEO-VB and St. In this approach, the chain length of precipitating oligomers as well as the nucleation period are regulated with the volume ratio ethanol/water (E/W) and the macromonomer concentration. The continuous phase polymerization and the polymerization in polymer particles govern the particle nucleation and the rate of polymerisation. The thickness (close-packed or flat conformation of PEO chains) of the particle shell (interfacial layer) is varied with the ratio water/ethanol and the macromonomer concentration as well. Furthermore, the interfacial layer conformation is expected to influence the entry of radicals into particles, the rate of polymerization and the colloidal stability of polymer dispersion.

Experimental

Materials. Commercially available styrene (St) (Fluka), vinylbenzyl alcohol (Dow Chemical Co.), benzoyl chloride, benzene, tetrahydrofuran, toluene and dimethyl sulfoxide (Fluka) were purified by distillation under reduced pressure and stored at 20 °C under nitrogen. Extra pure 2,2'-azoisobutyronitrile (AIBN, Fluka) and potassium hydride were used as supplied. Doubly distilled ethanol and water were used as a polymerization medium.

Synthesis of macromonomer. The vinylbenzyl-terminated polyoxyethylene macromonomer (PEO-VB) was prepared via anionic polymerization of ethylene oxide initiated by potassium vinylbenzyl alcoholate according to the previous procedure 7-9).

Recipe and Procedures. Batch dispersion copolymerizations of St and PEO-VB were carried out at 70 ° C. The recipe comprises 150 g water/ethanol and 15 g styrene. The amounts of PEO-VB and AIBN and the volume ratio water/ethanol (W/E) varied as shown later. The styrene conversion was determined by the gravimetric method. The particle size was determined by the transition electron microscopy (TEM) and light scattering method 10,11). Polymerization technique was same as described earlier 12). The molecular weight of polymer products was determined by the size exclusion chromatography in THF at 25 °C 13).

Results and Discussion

Rate of polymerization

The styrene conversion vs. time (t) curves of dispersion copolymerization of styrene (St) and p-vinylbenzyl-terminated polyoxyethylene (PEO-VB) macromonomer initiated by AIBN are shown in Figs. 1 and 2. They summarize the effect of the volume ratio ethanol/water (E/W) on the polymerisation for two PEO-VB concentrations. The S-shaped conversion vs. time curves appear at the low ratio E/W. The high ratio E/W is accompanied with the short nucleation period. The limiting conversion appears at ca. 80-90%. The conversion of the macromonomer was more difficult to estimate, and was not considered, except in a few cases. For instance, significant amount of residual macromonomer can be observed when the ratio E/W is high or when the amount or macromonomer initially introduced was high enough. SEC analysis allows us to estimate this residual quantity as 13% when E/W was 90/10 in the first series of experiment, and as 5% when, with a ratio of 70/30, the initial amount of macromonomer was 1.5 g, i.e. 10% of the amount of styrene. In a special run, the relative conversions of the styrene and of the macromonomer, have been compared: unfortunately, only qualitative data were obtained, due to the fact that convenient sampling is not safe in a reactor which was too small. It was observed that the consumption of the macromonomer was almost complete when the polymerisation rate reach a maximum value. The consequence is that at this moment there is no more possibility to produce new particles. A quantitative analysis, carried out by NMR showed that for a conversion of 69% for styrene, that of the PEO-VB was around 80%.

The limiting conversion (the very slow polymerisation at high conversion) can be attributed to the (partial) consumption of initiator (including the primary radical termination) and monomer, the immobilization of initiator and monomer (St) in the monomer/polymer particles and the increased continuous phase polymerization. The consumption of initiator (at longer polymerisation time) leads to the dead-end polymerisation because the half life time of AIBN at 70 °C is ca. 120 min [14]. Partitioning of St and PEO-VB between the continuous phase and the polymer particles varies with the volume ratio E/W [4]. With increasing the ratio E/W increases the total amount of monomer(s) in the continuous phase and therefore, the equilibrium distribution of the monomer toward the particle phase was more unfavourable. The preferential location of hydrophobic St in the polymer particles and hydrophilic PEO-VB

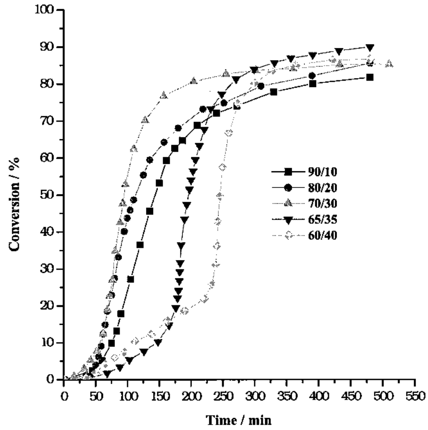

Fig. 1. Variation of monomer conversion with the reaction time and the volume ratio ethanol/water in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/ water, 15 g St, 0.3 g PEO-VB, and 0.306 g AIBN.

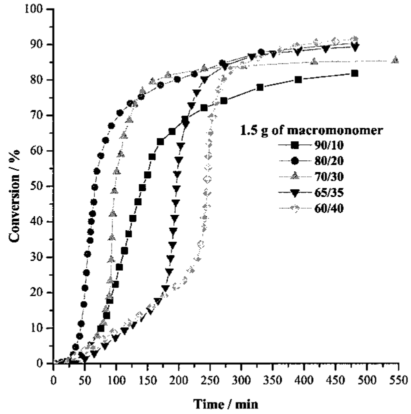

Fig. 2. Variation of monomer conversion with the reaction time and the volume ratio ethanol/water in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/ water, 15 g St, 1.5 g PEO-VB, and 0.306 g AIBN.

macromonomer in the continuous phase favour the slow solution (homo)polymerization of PEO-VB and fast polymerisation of St in the polymer particles. The monomer feed compositions in the continuous phase and monomer/polymer particles varies during the polymerization. The result is the shift in the composition of graft copolymers. The polymer which is formed in the polymer particles is almost pure polystyrene, and the macromonomer is introduced mainly through the capture of oligoradicals of the growing copolymer present in the continuous phase. Once captured, these oligoradicals can grew only through styrene polymerisation before they are mutually deactivated.

The dependence of the polymerization rate (R_p) vs. conversion is described by a curve with a maximum ($R_{p,max}$) at ca. 30-40% conversion (Figs. 3 and 4). First, the rate of polymerization (R_p) abruptly increased to the maximum ($R_{p,max}$) and then strongly decreased towards the end of polymerization. This differs from the classical dispersion copolymerisation [3,4] and the dispersion copolymerisation of PEO-MA macromonomers [15,16] where the maximal polymerisation rate appeared after the start of polymerisation and then it slightly decreased with increasing conversion. The two-rate intervals are attributed to two opposing effects: 1) the increased number of polymer particles (the transfer of reaction loci from the solution to the polymer particles) and 2) the decreased monomer concentration at the reaction loci [17].

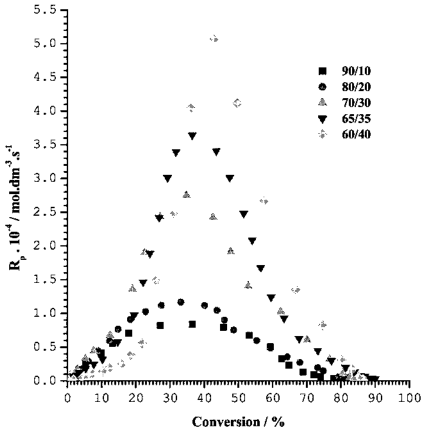

Fig. 3. Variation of the rate of polymerization with conversion and the volume ratio ethanol/water in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/ water, 15 g St, 0.3 g PEO-VB, and 0.306 g AIBN.

In emulsion polymerisation, the rate is proportional to the number of particles, and involves in normal conditions, only one active radical per particle. In dispersion polymerisation the situation is more complex, due to the large size of the particles, which may contain several active radicals. So, it is interesting to compare the maximum polymerisation rate with the number of particles. The data are reported in Tables 1-3.

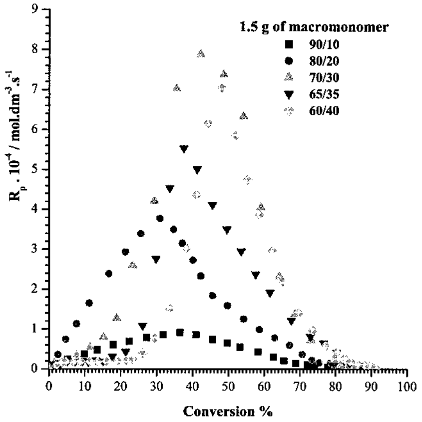

Fig. 4. Variation of the rate of polymerization with conversion and the volume ratio ethanol/water in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/water, 15 g St, 1.5 g PEO-VB, and 0.306 g AIBN.

Although the correlation is not so direct, there is obviously an increase of the maximum rate with the increasing number of particles in most cases. But also some other parameters are to be taken into account. The rate is depending also on the average number of radicals working simultaneously in the same particle, and that number is depending at least on 3 parameters: i) the surface area of the particles for capturing the radicals formed in the continuous medium, ii) the rate of production of these radicals, iii) the termination rate inside the particles.

The short nucleation period (at large E/W ratio) is typical for the dispersion polymerisation while the long nucleation period (at low E/W ratio) is typical for the emulsifier-free emulsion polymerisation. In the former the coagulative nucleation is operative while in the latter the homogeneous nucleation. The polymerisation starts in solution (reactants are dissolved in the continuous phase) and therefore the solution polymerization governs the polymerization process at low conversion. The accumulation of polymer particles leads to the transfer of reaction loci from the continuous phase to the polymer particles. The kinetic data (Figs. 3 and 4) show that the efficiency of the transfer of reaction loci from the solution system to the polymer particles (compartmentalized reaction loci) increases with increased water amount. The polymerization rate increased with decreasing the ratio E/W. The similar trend in the polymerisation rates vs. the polarity of the reaction media was reported in [4)]. At high ratio E/W the monomer accumulates in the continuous phase while at low E/W most of hydrophobic monomer is located in the monomer-polymer particles [4)]. In the former the polymerisation could proceed under the monomer-starved condition (slow polymerisation) while in the latter under the monomer-saturated condition (fast polymerisation) in the monomer/polymer particles.

The solubility parameter δ [(cal/cm^3)$^{0.5}$] was estimated to increase from 12 to 15.4 with decreasing the ratio E/W from 90/10 to 60/40. Figs. 1 and 2 show that the length of nucleation period increased with increasing the solubility parameter. The values of δ were calculated as the volume weighted average of the solubility parameters of the cosolvents and styrene 16). The increased solvency of the reaction medium (water) towards the growing radicals (PEO macromonomer end unit) increases the critical molecular weight above which the growing polymer chains precipitate from the continuous phase and aggregate to organized aggregates or enter the polymer particles. Under the high solvency, the graft copolymer molecules can associate to primary particles able to absorb monomer and continue in polymer growth. The increased solvency (the solubility parameter) was accompanied with the increased weight swelling ratio 5). The higher the water content (smaller E/W ratio), the higher the monomer (St) swelling of the resulting particles.

The conversion at which $R_{p,max}$ appears increases with decreasing the E/W ratio and PEO-VB concentration (Tables 1 and 2). The higher the solvency of continuous phase and macromonomer concentration, the longer the nucleation period or the larger Conv.$_{Rp,max}$.

The initial abrupt increase in the polymerization rate can be attributed to the sharp accumulation of polymer particles (compartmentalized growing radicals). The increase in R_p is inversely proportional to the ratio E/W. This is connected with increased monomer concentration (the weight ratio of monomer to polymer) in the polymer particles. The strong decrease in R_p after Conv.$_{Rp,max}$ indicates the strong deactivation of reaction loci. This can be discussed in terms of the decreased concentration of monomer and increased pseudo-bulk kinetics (accumulation of radicals in large polymer particles). At high conversion the solution polymerization of hydrophilic macromonomer increases due to the swelling of hydrophobic polymer particle with the hydrophobic monomer (St). The formation of more hydrophilic radicals disfavours the entry of radicals into the hydrophobic polymer particles. The depressed formation of graft copolymer decreases the additional stabilization of growing polymer particles. The limited flocculation of polymer particles decreases the polymerization rate. PSt or copolymer rich in styrene units was confirmed by full adsorption/desorption SEC formed in the dispersion copolymerisation of styrene and PEO-MA macromonomer 18,19).

The rate of polymerization increases with increasing PEO-VB concentration (Figs. 5 and 6). The reaction order y = 0.27 ($R_{p,max}$ vs. $[PEO\text{-}VB]^y$) deviates from both the solution (macromonomer acts as (co)monomer) and micellar (macromonomer or its graft copolymer acts as stabilizer) polymerisations. The reaction order y is a complex function of two contributions. The solution copolymerisation of styrene and PEO-VB generates the surface active graft (St-g-PEO) copolymer product which at low conversion takes part in the particle nucleation (associates to organized aggregates - micelles) and later is adsorbed by the growing polymer particles (additional stabilization). The contribution of slow solution polymerisation to the overall reaction yield is very low or even negligible. However, the graft copolymer molecules formed in the solution polymerization are responsible for the formation of polymer particles and their stabilization. The reaction order y can be taken as a measure of surface activity of graft copolymer. In the dispersion copolymerization of methacryloyl-terminated PEO (PEO-MA) macromonomer and styrene, the reaction order y ($R_{p,max}$ vs. $[PEO\text{-}MA]^y$) increased from 0.5 to 4 with increasing [PEO-MA] 16). This was paralleled with the increased particle number. Relatively small particles with the average particle diameter ca. 50 – 100 nm were formed. The much larger particle with diameter 500 – 1000 nm are formed in the present St/PEO-VB system. The low stabilization activity of PEO-VB/St graft copolymer can be attributed to the high hydrophobicity of graft copolymer and so to its burying in the polymer particle matrix. The PEO-VB/St graft copolymer was well dissolved in all common organic solvents. This was not the case for PEO-MA/St graft copolymers 20).

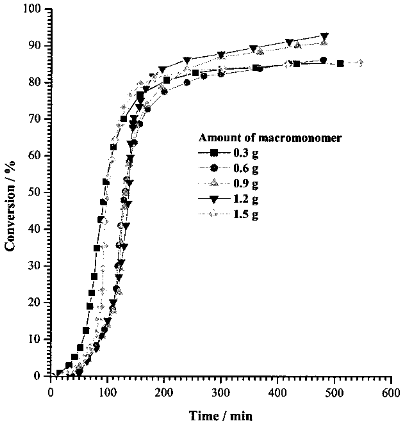

Fig. 5. Variation of monomer conversion with the reaction time and the PEO-VB concentration in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/water, 15 g St, the volume ratio E/W (70/30) and 0.306 g AIBN.

PEO-MA/St graft copolymer was much better colloidal stabilizer than PEO-VB/St graft copolymer [21].

The more packed PEO chains (high macromonomer concentration) makes barrier for entering radicals to the polymer particles [22,23]. This decreases the radical flux into the polymer particle and the rate of polymerisation. On the contrary, the colloidal stability of polymer particles increases with the packing density of PEO chains and so the polymerization rate. The flat conformation of PEO chains is expected to appear in ethanol while the highly packed one appears in water. In the former the polymer particles flocculate while in the latter (water-rich system) the polymer particles are more stable.

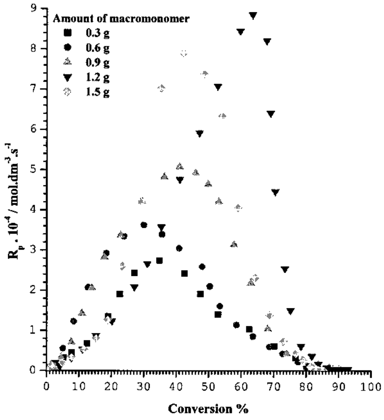

Fig. 6. Variation of the rate of polymerization with conversion and PEO-VB concentration in the dispersion (co)polymerization of St and PEO-VB at 70 °C initiated by AIBN initiator. The recipe: 150 g ethanol/ water, 15 g St, the volume ratio E/W (70/30), and 0.306 g AIBN.

The rate of dispersion copolymerisation of PEO-MA and St increased with increasing AIBN concentration for two different macromonomer concentrations (Fig. 7) [9]. $R_{p,max}$ was estimated to increase with increasing [AIBN] for two different PEO-VB concentrations (0.3 g and 1.5 g):

$$R_{p,max} \propto [AIBN]^{0.31} \text{ and } R_{p,max} \propto [AIBN]^{0.39} \qquad (1)$$

The reaction orders 0.31 and 0.39 deviates from the kinetic model of dispersion polymerisation (0.50) [24]. The increase of $R_{p,max}$ with increasing [AIBN] results from the increased number of radicals per particle and particle surface area (see later). The increased number of radicals per large particle is accompanied with the pseudo-bulk kinetics and/or the gel effect [17,25]. The gel effect depresses the dependence of R_p on the initiator concentration.

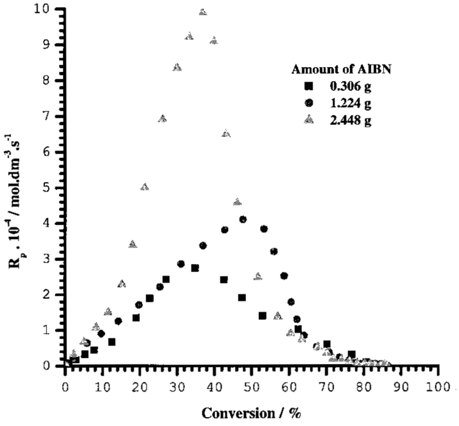

Fig. 7. Variation of the rate of polymerization with conversion and AIBN concentration in the dispersion (co)polymerization of St and PEO-VB at 70 °C. The recipe: 150 g ethanol/ water, 15 g St, the volume ratio E/W (70/30), 0.3 g PEO-VB and 0.306 g AIBN.

Colloidal and molecular weigh parameters

The particle size decreases and particle concentration increases with increasing the amount of water and the decrease is more pronounced at higher concentrations of PEO-VB (Tables 1 and 2). The increased amount of water is paralleled with both the prolonged nucleation period and increased number of final polymer particles. These findings are connected with the increased solvency of the reaction medium. The PEO chains more

Table 1. Variation of colloidal and molecular weight parameters with the volume ratio ethanol/water (E/W) in the dispersion (co)polymerization of St and PEO-VB. [a)]

E/W (v/v)	D_n (nm)	$N_p \times 10^{14}$ /dm^3	D_n/D_w	$M_n \times 10^{-3}$	M_w/M_n	$R_{p,max}$ (mol.dm^{-3}.s^{-1})	Conv.$_{Rp,max}$ (%)
90/10	-	-	-	15	6.5	0.9	33
80/20	1150	0.87	1.01	23	4.8	1.2	33
70/30	890	1.92	1.1	21	5.2	2.6	35
65/35	840	2.2	1.03	32	4.3	3.7	37
60/40	820	2.6	1.4	32	4.6	5.1	45

a) The recipe: 150 g ethanol/ water, 15 g St, 0.3 g PEO-VB, and 0.306 g AIBN.

extended into water than into ethanol are responsible for the increased colloidal stability of polymer particles or larger particle concentration.

Table 2. Variation of colloidal and molecular weight parameters with the volume ratio ethanol/water (E/W) in the dispersion (co)polymerization of St and PEO-VB. [a)]

E/W (v/v)	D_n (nm)	$N_p \times 10^{14}$ /dm^3	D_n/D_w	$M_n \times 10^{-3}$	M_w/M_n	$R_{p,max}$ (mol.dm^{-3}.s^{-1})	Conv.$_{Rp,max}$ (%)
90/10	-	-	-	14	8.9	0.8	36
80/20	1275	0.67	1.03	14.5	8.3	3.8	31
70/30	565	7.5	1.1	31	3.5	7	45
65/35	650	5.2	1.05	38	5.0	5.6	38
60/40	570	8.0	1.6	38	5.5	6	50

a) The recipe: 150 g ethanol/ water, 15 g St, 1.5 g PEO-VB and 0.306 g AIBN.

The particle size (D) and the number of polymer particles (N_p) slightly vary with increasing PEO-VB concentration (Table 3):

$$D \propto [\text{PEO-VB}]^{-0.3} \quad \text{and} \quad N_p \propto [\text{PEO-VB}]^{0.92} \qquad (2)$$

The value of exponent (0.93) is larger than 0.56 for the dispersion copolymerization of PEO macromonomer and butyl methacrylate [2,26)] but smaller than 3 for the dispersion copolymerization of styrene and PEO-MA [16)]. The exponents 0.3-0.9 for saturated nonionic emulsifiers [27)] are comparable with 0.93. These findings indicate that PEO-VB (its graft copolymer) stabilizer is comparable with the saturated nonionic emulsifiers but less efficient than the PEO-MA/St graft copolymer. This can result from burying the more hydrophobic PSt-VB/St graft copolymer in the polymer matrix.

The particle size the particle number vary slightly with increasing AIBN concentration (Table 4):

$$D \propto [\text{AIBN}]^{-0.18} \quad \text{and} \quad N_p \propto [\text{AIBN}]^{0.7} \quad (0.3\ \text{g PEO-VB}) \qquad (3)$$

$$D \propto [\text{AIBN}]^{-0.11} \quad \text{and} \quad N_p \propto [\text{AIBN}]^{0.33} \quad (1.5\ \text{g PEO-VB}) \qquad (4)$$

In the dispersion polymerisation, contrary to emulsion polymerisation, an increase in the initiator concentration led to fewer polymer particles [4)]. This was discussed in terms of the formation of smaller polymers with increased solubility in the reaction medium. The increased solubility of polymer decreased the adsorption of small chains by particle surface. The strong deviation from the kinetic model can be attributed to the different stabilization mechanism. The PEO chains are chemically bound to the particle surface while in the classical dispersion polymerization the stabilizer is adsorbed on the particle surface. This can vary the entry mechanism of radicals into particles. In the former the PEO surface chains can not be replaced by new entering radicals containing PEO chain. This is, however, possible in the latter. The decreased entry of (graft copolymer) oligomers into the particles can promote their association to new polymer particles.

Table 3. Variation of colloidal and molecular weight parameters with the PEO-VB concentration in the dispersion (co)polymerization of St and PEO-MA. [a)]

PEO-VB (g)	D_n (nm)	N_p x 10^{14} /dm^3	D_n/D_w	M_n x 10^{-3}	M_w/M_n	$R_{p,max}$ ($mol.dm^{-3}.s^{-1}$)
0.3	890	1.92	1.04	21	5.2	2.8
0.6	760	3.1	1.14	25	5.9	3.4
0.9	600	6.7	1.05	29	6.9	5
1.2	600	6.7	1.09	29	7.2	6.8
1.5	565	7.5	1.1	31	7.6	7.8

a) The recipe: 150 g ethanol/ water, 15 g St, the volume ratio E/W (70/30) and 0.306 g (0.18 mM) AIBN.

The interaction of PEO chains with water decreases with temperature. Oxyethylene groups form hydrogen bonds with water. As temperature or ethanol extent is increased, these relatively weak bonds begin to dissociate and water molecules are gradually driven out of the (shell) region occupied by POE chains. The length and excluded volume of PEO per amphiphile in the interfacial layer are decreased. The temperature at which clouding of the emulsifier solution occurs depends on the structure of polyoxyethylenated emulsifier and increases with the length of PEO chains or its content in copolymer. For example, the cloud point for ethoxylated nonylphenols with an average of 30 - 50 oxyethylene units per molecule was reported to be 65-75 °C [28)]. The polymerization temperature 70 °C can be close to the cloud point temperature of graft copolymer (stabilizer). Under such conditions, the flat configuration of interfacial layer appears and most of graft copolymer is dissolved in the monomer phase (monomer/polymer particles). The similar behavior with configuration of PEO chains can be expected with increasing fraction of ethanol.

Table 4. Variation of colloidal and molecular weight parameters with the PEO-VB concentration in the dispersion (co)polymerization of St and PEO-MA. [a)]

AIBN (mM)	D_n (nm)	$N_p \times 10^{14}$ /dm^3	D_n/D_w	$M_n \times 10^{-3}$	M_w/M_n
1.86 [b)]	890	1.9	1.04	21	5.2
7.4	610	6.2	1.03	13	5.3
14.9	550	8.0	1.03	8.4	5.4
2.9 [c)]	565	7.5	1.1	31	3.6
8.0	500	12.0	1.04	16	5.8
16.0	450	16.0	1.08	13	6.4

a) The recipe: 150 g ethanol/water, 15 g St, the volume ratio E/W (70/30) and 0.306 g AIBN, b) 0.3 g PEO-VB, c) 1.5 g PEO-VB.

Tables 1 - 4 show that the molecular weight of graft copolymers is relatively low. The molecular weight of polymer varies with the concentration of monomer and initiator and the reactivity of (co)monomers. One of the possible factors for the formation of low molecular weight polymers is the low reactivity of macromonomer (sterically hindered reaction loci). This depresses propagation but favours more side reaction such he chain transfer events [29)].

The apparent number-average molecular weight (M_n) was found to increase with increasing volume fraction of water (n_w) and the increase was more pronounced for larger PEO-VB concentration (Tables 1 and 2):

$$M_n \propto n_w^{0.64} \text{ and } M_n \propto n_w^{0.94} \qquad (5)$$

These findings can be discussed in terms of increased solvency of the reaction medium to the growing radicals [3,4)] and the increased contribution of polymerisation within the smaller particles (the more compartmentalized reaction loci) [25,30)]. The solvency of medium to the growing radicals increases also with increasing PEO-VB concentration (E/W, 70/30) (Table 3):

$$M_n \propto [\text{PEO-VB}]^{0.28} \qquad (6)$$

The increased M_n is also paralleled with the increased particle concentration or the polymerization under restricted radical termination.

The two possible reaction loci (the continuous phase and the polymer particles) suggest the formation of small and larger polymers. The present data show that molecular weight distribution (MWD) is very broad. MWD decreased with increasing solvency of the reaction medium and the decrease was more pronounced for larger PEO-VB concentration (Tables 1 and 2). Table 3 confirms the increase in MWD with increasing macromonomer concentration. MWD increased with increasing AIBN and particle concentrations.

The molecular weight of PEO-VB/St graft copolymer increased with increasing AIBN concentration (Table 4):

$$M_n \propto [\mathrm{AIBN}]^{0.42} \text{ and } M_n \propto [\mathrm{AIBN}]^{0.44} \tag{7}$$

The reaction orders 0.42 and 0.44 strongly deviate from both the solution and dispersion polymerizations. In the former, for example, the molecular weight is inversely proportional to the initiator concentration. The mechanism polymer generation, thus, is somehow connected with the nucleation period and the size and number of particles. The mobility of PEO chains is inversely proportional to the molecular weight of PEO-VB/St graft copolymer. At the small PEO graft copolymer, PEO chains can diffuse more easily to the particle surface, take part more efficiently on the formation of close-packed interfacial layer and form more stable polymer particles 31). On the contrary, the increased immobilization of PEO chains of large polymer in the polymer matrix is accompanied with formation of less stable polymer particles or coarse polymer dispersion. The radical flux into polymer particle or the radical entry coefficient is inversely proportional to the particle size 32). The molecular weight of polymer is inversely proportional to the particle size. The small particles or larger number of particles are formed at high [AIBN]. The pseudo-bulk kinetics become more pronounced as the particle size increases. The increased molecular weight with increasing initiator concentration confirms the fact that the polymer product is mainly generated in polymer particles.

The foregoing discussion indicates that the final polymer is mainly produced in the polymer particles (reduced termination). However, the small molecular weight (M_n) of polymer somehow disfavors the reduced termination approach. The molecular weights of graft copolymers were determined by size exclusion chromatography (SEC) in which the molecular weight is proportional to the size of graft copolymer molecules. It is known that the absolute M_n of graft copolymers is difficult to assess by SEC because of their branched structure, chemical composition heterogeneity, partial adsorption of copolymer molecules on the column package, etc. and difficulties to find an ideal solvent for graft copolymer and a strong inter- and intramolecular association [18). The molecular weight of amphiphilic graft polymers estimated by SEC can be strongly underestimated due to intramolecular association of graft copolymer molecules [1,2,20,29).

Conclusion

The conversion time curve consists of three regions: 1) the nucleation period, 2) the fast polymerisation and 3) the slow polymerisation - limiting conversion. The length of nucleation period is inversely proportional to the volume ratio ethanol/water (E/W). The limiting conversion does not depend on PEO-VB concentration or the ratio E/W. The short nucleation is typical for dispersion polymerization (coagulative nucleation) while the long nucleation period for the emulsifier-free emulsion polymerization (the homogeneous nucleation). The dependence of the polymerization rate (R_p) vs. conversion is described by a curve with two-rate intervals which is assumed to be a result of two opposing effects: 1) the increase of particle number and 2) the decrease of monomer concentration at the reaction loci. The rate of polymerization increases with increasing PEO-VB concentration as a result of increased particle concentration. The maximal polymerisation rate ($R_{p,max}$) increases with increasing AIBN concentration and the increase was independent of the ratio E/W. The particle number slightly increased with increasing PEO-VB and AIBN concentration. The molecular weight of polymer product increased with increasing the amount of water, initiator, macromonomer and particle concentration. The reduced radical flux per particle and radical termination result in the formation of larger polymers. The broad molecular weight distribution results from two contributions: the polymerisation solution and polymer particles and their variation with conversion.

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