# Effects of the Initiator Type on the Dispersion Copolymerization of Poly(ethylene glycol) Macromonomer and Styrene[†]

Ignac CAPEK,* Medyan RIZA, and Mitsuru AKASHI

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, 1-20-40 Korimoto, Kagoshima 890, Japan

ABSTRACT:  The dispersion copolymerization of methacryloyl terminated poly(ethylene glycol) (MMA–PEG) macromonomer and styrene initiated by a water- and oil-soluble radical initiator was investigated by a conventional gravimetric method at 60°C. The rate of polymerization and number of radicals per particle were found to decrease with conversion and decrease was more pronounced with the oil-soluble initiator. On the other hand, the size, number of particles and molecular weight of polymers increased with conversion and increase was more pronounced with the water-soluble initiator. The experimental data indicate that the formation of radicals in the continuous phase plays a dominant role in the growth of polymer chains and polymer particles. The distribution of the oil-soluble initiator between continuous and monomer/polymer phases leads to the generation of radicals also in the monomer/polymer phase and to the increased termination events. The generation of radicals and the termination of growing radicals in polymer particles are promoted through the cage effect mechanism.
    KEY WORDS    Poly(ethylene glycol) Macromonomer / Dispersion / Copolymerization / Polymer Particle / Number of Particles / Water- and Oil-Soluble Initiator / Termination / Cage Effect /

The kinetics of emulsion polymerization that uses oil-soluble initiators has given rise to much contraversy because contrary to what is expected, the behavior is similar to that found for water-soluble initiators.[1–6] However, these authors proposed two mechanisms for the production of radicals; 1) in the monomer-swollen polymer particles formed radicals desorb to the continuous phase and 2) in the continuous phase formed radicals are generated from the fraction of the oil-soluble initiator dissolved in water.

However, to our knowledge no attention has been paid to the effects of the type of initiator on the kinetics of the dispersion polymerization or copolymerization of macromonomers.

If the initiator is soluble in the continuous phase, the concentrations of radicals are functions of initiator concentration, decomposition rate constant of initiator and initiator efficiency. The mechanism of radical formation and entry of radicals into polymer particles should be similar to those in the emulsion polymerization.[7] If the initiator is distributed between polymer particles and continuous phase, the rate of initiation should be a function of initiator concentration in the continuous phase[4,5] and/or the fraction of desorbed primary radicals from two polymer particles.[1,2]

In the present paper, water/ethanol dispersion copolymerizations were carried out with the different types of initiator keeping the rate

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of initiation constant to elucidate the main locus of radical formation and applicability of the present models for the radical formation. For this purpose we followed the radical copolymerization of the amphiphilic PEG macromonomer having a methyl methacrylate end group and low molecular weight hydrophobic styrene monomer using a radical initiator soluble in the water/ethanol phase only and the other one soluble in both the water/ethanol and monomer/polymer phases.
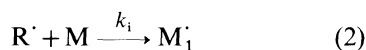
## THEORY

In the water/ethanol dispersion polymerization, the thermal decomposition of the continuous phase soluble initiator generates primary radicals in the continuous phase. However, the major locus of polymerization was suggested to be the interior of the polymer particles.[8] The oil-soluble initiator is supposed to generate radicals also in the monomer/polymer phase.[1,2]

The following reaction schemes are proposed for the ethanol/water dispersion polymerization initiated by

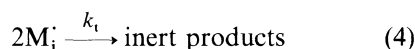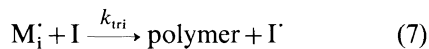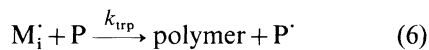a) the continuous phase-soluble initiator[7,9]:
Initiator decomposition

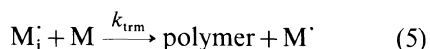$$I \xrightarrow{k_d} 2R^{\cdot} \tag{1}$$

Initiation

$$R^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot} \tag{2}$$

Propagation

$$M_i^{\cdot} + M \xrightarrow{k_p} M_{i+1}^{\cdot} \tag{3}$$

Termination

$$2M_i^{\cdot} \xrightarrow{k_t} \text{inert products} \tag{4}$$

Chain-transfer reactions

$$M_i^{\cdot} + M \xrightarrow{k_{trm}} \text{polymer} + M^{\cdot} \tag{5}$$

$$M_i^{\cdot} + P \xrightarrow{k_{trp}} \text{polymer} + P^{\cdot} \tag{6}$$

$$M_i^{\cdot} + I \xrightarrow{k_{tri}} \text{polymer} + I^{\cdot} \tag{7}$$

Entry

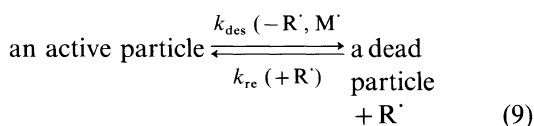$$M_j^{\cdot} + \text{particle} \xrightarrow{k_e} \text{activation or deactivation of particle} \tag{8}$$
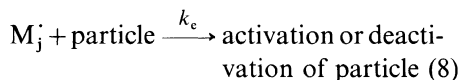
b) the oil-soluble initiator[1]: The polymerization principally includes the kinetic events given by eq 1—7 (for the monomer/polymer phase) and also the following step
Radical desorption (re-entry)

$$\text{an active particle} \underset{k_{re} (+R^{\cdot})}{\overset{k_{des} (-R^{\cdot}, M^{\cdot})}{\rightleftarrows}} \text{a dead particle} + R^{\cdot} \tag{9}$$

Here I is the initiator, $R^{\cdot}$ the primary radical formed by the decomposition of initiator, M the monomeric unit, $M^{\cdot}$ the monomeric radical, $P^{\cdot}$ the polymeric radical, $I^{\cdot}$ the radical formed by the chain-transfer to initiator, $M_i^{\cdot}$ the growing radical with with initiator fragment (soluble or insoluble in the continuous phase, $j$ the number of monomer units in oligomer radical before it enters the particle, $i = 0, 1, 2, \cdots, j$), $M_j^{\cdot}$ the continuous phase free radical, $k_d$ the first-order initiator decomposition rate constant, $k_i$ the initiation rate constant, $k_p$ the propagation rate constant of the polymeric radical, $k_t$ the termination rate constant of the polymeric radical, and $k_{trm}$ the monomer chain-transfer rate constant, $k_{trp}$ the polymer chain-transfer rate constant, $k_{tri}$ the initiator chain-transfer rate constant, $k_{des}$ the desorption rate constant, $k_e$ the entry rate constant, and $k_{re}$ the re-entry constant.

The first microscopic event, the formation of primary radicals by the decomposition of initiator, must occur to start the growth of macromolecule. This event governs the rate of initiation and subsequently the rate of

polymerization. The rate of initiation is known to be a function of the initiator efficiency ($f$), the initiator decomposition rate constant ($k_d$) and the initiator concentration ([I]) and can be calculated using the following equation

$$R_i = 2 \cdot f \cdot k_d \cdot [I] \tag{10}$$

In the dispersion polymerization the rate of radical (primary particle) formation, $R$, influences strongly particle nucleation as well as the polymerization rate and depends on the rate of initiation. The rate of primary particle formation can be calculated by the following equation

$$R = R_i \times N_A \tag{11}$$

where $N_A$ is the Avogadro's number.

## EXPERIMENTAL

### Materials

Commercially available styrene (St) monomer and initiator VA-061 (2,2'-azobis[2-(2-imidazolin-2-yl)-propane), water- and ethanol soluble initiator, VA) and dibenzoyl peroxide (BPO, the oil-soluble initiator) were purified by usual methods. Solvents such as benzene, ethanol and water were twice distilled before use. Methacryloyl terminated poly(ethylene glycol) (MMA–PEG, $M_n = 1000$) was supplied by Nippon Oil and Fats Co.

### Polymerization Procedure

Batch copolymerizations of MMA–PEG macromonomer and styrene were carried out at 60°C. In all runs, the recipe containing 5 ml of ethanol–water (4 : 1, v/v), 1.11 g of styrene, 0.3 g of MMA–PEG and 0.0273 g of VA or 0.0273 g of BPO (initiator) was used. The polymerization technique used is described in detail elsewhere.[10] The conversion of monomers was determined by gravimetry and GPC. The rate of polymerization is expressed in moles of monomer converted to polymer in 1 dm³ of the continuous phase (ethanol/water) per sec. The concentration of monomer,

initiator and polymer particles is expressed in moles or the number of particles in 1 dm³ of the continuous phase.

### Polymer and Latex Characterization

The polymer latexes were freed of monomer, macromonomer, initiator, and low-molecular byproducts by dialysis according to the method described previously.[11] Particle size measurements were done by electrone microscope, Hitachi H-7010A, was used. The number of particles were calculated according to the method described in ref 4, 8. Number-average molecular weights of macromonomers and copolymers were determined by a vapor pressure osmometer (Corona Model 117) and by gel permeation chromatography with a Simadzu LC-6A system equipped with Shodex column (AC-8034, 8 × 500 mm).[12]

## RESULTS AND DISCUSSION

### The Rate of Polymerization

The conversion *versus* time data of the dispersion copolymerizations of styrene with MMA–PEG macromonomer initiated by BPO and VA are shown in Figure 1. The conversion curve with VA is nearly linear up to 30 or 40%
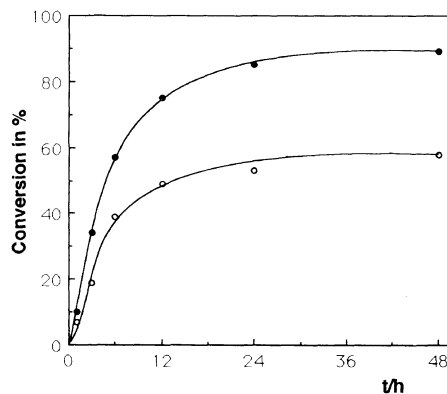


**Figure 1.** Variation of monomer conversion in the dispersion copolymerization of styrene and MMA–PEG with reaction time and type of initiator. Recipe: 5 ml ethanol–water (4 : 1, v/v), 1.11 g styrene 0.3 g MMA–PEG and 0.0273 g BPO (or VA), temp, 60°C. VA (●) and BPO (○).

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**Table I.** Variation of the rates of polymerization in the dispersion copolymerization of styrene and MMA–PEG macromonomer with the type of initiator and conversion

| Conversion | $R_p \times 10^{5\,a}/$ mol·dm$^{-3}$·s$^{-1}$ | | | $R_{pp} \times 10^{22\,b}/$ mol·s$^{-1}$·particle$^{-1}$ | | $R_{ppf} \times 10^{22\,c}/$ dm$^3$·s$^{-1}$·particle$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| % | a$^d$ | b$^d$ | a/b$^d$ | a$^d$ | b$^d$ | a$^d$ | b$^d$ | a/b$^d$ |
| 10 | 9.5 | 5.3 | 1.9 | 23.8 | 5.9 | 5.1 | 1.3 | 4.0 |
| 30 | 9.0 | 4.0 | 2.2 | 7.8 | 2.4 | 2.1 | 0.66 | 3.2 |
| 40 | 8.0 | 2.0 | 4.0 | 5.2 | 1.1 | 1.67 | 0.35 | 4.8 |
| 50 | 6.5 | 0.3 | 21.7 | 3.4 | 0.14 | 1.3 | 0.05 | 26.0 |
| 60 | 5.1 | <0.1 | >50.0 | 2.3 | 0.05 | 1.1 | 0.02 | 55.0 |
| 70 | 1.6 | <00.1 | | 0.7 | — | 0.45 | | |

$^a$ Rate of polymerization.
$^b$ Rate of polymerization per particle (number of particles are listed in Table II).
$^c$ Fractional rate of polymerization calculated under the assumption that the equilibrium monomer concentration decreases linearly with conversion, i.e., at conversion close to zero $[M]_p = 5.2$ mol·dm$^{-3\,13,14}$ and chose to 100% is zero.
$^d$ a, with VA; b, with BPO, a/b the ratio of data given in the columns a and b.

conversion and then slowly levels off. On the other hand, the shape of conversion curve with BPO resembles the curve for the precipitation or the dead-end polymerization. The rates of polymerization obtained at a given conversion are expressed as a function of the type of initiator and conversion in Table I. These results show that the rates of polymerization in the VA system decrease only slightly with conversion while those for the BPO system decrease strongly.

The extrapolation of the ratio $R_p$(VA)/ $R_p$(BPO) to zero conversion gives the value of this ratio close to 1. In both systems the rates of polymerization at zero conversion are nearly the same. The same rates of initiation $(R_i = 8.4 \times 10^{-8}$ mol·dm$^{-3}$·s$^{-1}$ (BPO) and $R_i = 4.4 \times 10^{-8}$ mol·dm$^{-3}$·s$^{-1}$ (VA),[8]), thus, should lead to the same rates of polymerization in the medium and high conversions. The values of $R_i$ also indicate that the rate of polymerization should be slightly higher for the BPO system. The experimental results show that the reverse is true. The rate of polymerization at medium or high conversion with BPO is lower than that with VA even if the half life time of BPO initiator is higher than that of VA.[15,16] For example, with VA the

copolymerization reaches 90% conversion after 24 h while that with BPO only 50% conversion.

It was reported that homogeneous polymerizations and copolymerizations of macromonomers proceed under stationary conditions and the rates are lower than those in the polymer particles.[8,17,18] These data indicate that variation in polymerization rates with time should be ascribed to the kinetic events proceeding mainly in the polymer particles (Table I).

In the VA system, the formation of the new monomer/polymer phase leads to increase of the initiator concentration in the continuous phase while the total volume of the continuous phase decreases due to the transfer of the monomer to the polymer phase. Thus, this variation in the initiator concentration should lead to increase of the rate with conversion. In the BPO system the formation of monomer/polymer phase leads to transfer of both the monomer and initiator to the monomer/ polymer phase. In the latter system, the amount of BPO gradually decreases in the continuous phase. The monomer-swollen polymer particles are saturated with BPO molecules. If we consider that the rate constant for the entry of

BPO molecules into the polymer particles, $k_{e,BPO}$, is near the diffusion value of $10^{-9}$—$10^{10}\,dm^3\cdot mol^{-1}\cdot s^{-1}$,[19] then the amount of initiator per unit volume should be approximately the same in the both phases. The same consideration should be valid also for the non-polar hydrophobic styrene monomer molecules. In the case of styrene, the diffusion of the monomer to the polymer particles is favored by the same nature of the monomer and polymer phases (non-polar components).[20] Thus, at 40 or 50% conversions about 20% of the total initiator amount should be located in the polymer phase and the rate of initiation in the continuous phase should decrease to $6 \times 10^{-8}\,mol\cdot dm^{-3}\cdot s^{-1}$. The decrease in $R_i$ is not significant and therefore the rate of radical entry and the rate of polymerization should be kept on the high level. If we take into account that the transfer of macromonomer to the polymer particle phase decreases the viscosity of the continuous phase, then increase of the initiator efficiency and the rate of initiation is expected.[21] Thus, these factors are in favor of the continuous phase polymerization and the rate of polymerization should be high and the same in both systems. The experimental data, however, show that the rate of polymerization decreases with conversion and the decrease is stronger in the BPO system. With BPO the polymerization process nearly stops at 40 or 50%. This behavior somewhat disfavors the dominant role of the radical formation in the continuous phase. Therefore, the present kinetic data should be discussed also in terms of the contribution of kinetic events in the polymer particles, such as: 1) the change in the hydrophobicity of oligomer radicals with conversion, 2) the radical termination and 3) the desorption of radicals from the polymer particles (see later).

It has been recognized[22] that, on thermodynamic grounds, hydrophilic primary radicals do not diffuse spontaneously from the polar (aqueous or ethanol) continuous environment to the (nonpolar) oil-phase. Thus, also in the ethanol/water dispersion polymerization the addition of styrene to the primary radicals derived especially from VA would be required to promote this transfer. It was observed[8] that with increasing conversion descrease, the fraction of styrene monomer in the monomer mixture (the amount of styrene units in copolymer increased nearly 5 times from 10 to 30% conversion). The accumulation of hydrophilic MMA–PEG macromonomer promotes the formation of the hydrophilic oligomer radicals with high surface activity but low penetration into the polymer particle core. The addition of hydrophilic monomer should decrease the radical entry rate into the particle and its penetration into the particle core. The contribution of the slow continuous phase polymerization may also increase at the same time. The rate of polymerization per particle was found to decrease with conversion and the decrease was more pronounced in the BPO system (Table I).

The weight ratio of monomer to polymer for polystyrene particles swollen by styrene was reported to be 1.3.[13,14] Thus, the polymerization proceeds under a condition of 40% conversion at which termination reactions should already be suppressed. Under this condition, increase of both the radical concentration and the rate of polymerization from the start of polymerization is expected. In other words, polymerization should proceed under gel effect conditions. The experimental results show that the reverse is true, *i.e.*, the rate of polymerization decreases with conversion. Thus, the strong chain-transfer to macromonomers[8,21,23] and decreased reactivity of the propagating radicals[21] may depress the gel effect.

Variation in monomer concentration with conversion is the same in both systems and therefore the difference in rates should be discussed in terms of different mechanisms of radical termination and/or radical generation.

**Table II.** Variation of particle size and number of particles in the disperion copolymerization of styrene and MMA–PEG macromonomer with the type of initiator and conversion

| Conversion % | $D^a/$ nm | | | $dD/dt \ (\times 10^4)^b/$ nm·s$^{-1}$ | | | $N \times 10^{-14c}/$ cm$^3$ | | | $dN/dt \ (\times 10^{-10})^d/$ (particles·s$^{-1}$·cm$^{-3}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a$^e$ | b$^e$ | a/b$^e$ | a$^e$ | b$^e$ | a/b$^e$ | a$^e$ | b$^e$ | a/b$^e$ | a$^e$ | b$^e$ | a/b$^e$ |
| 10 | 105 | 77 | 1.36 | 5.7 | 14.0 | 0.4 | 0.4 | 0.9 | 0.44 | 2.0 | 1.0 | 2.0 |
| 30 | 108 | 95 | 1.14 | 4.8 | 8.6 | 0.56 | 1.15 | 1.7 | 0.68 | 1.34 | 0.3 | 4.5 |
| 40 | 109 | 99 | 1.1 | 4.2 | 5.8 | 0.72 | 1.55 | 1.9 | 0.82 | 1.0 | 0.16 | 6.2 |
| 50 | 109 | 106 | 1.03 | 4.2 | 0.8 | 5.2 | 1.9 | 2.1 | 0.9 | 0.91 | 0.03 | 30.3 |
| 60 | 111 | 108 | 1.03 | 3.4 | | | 2.2 | 2.2 | 1.0 | 0.4 | | |
| 70 | 113 | | | 2.9 | | | 2.3 | | | 0.14 | | |
| 80 | 117 | | | 1.3 | | | 2.3 | | | | | |
| 90 | 125 | | | | | | 2.3 | | | | | |

$^a$ Particle diameter.
$^b$ Rate of particle diameter growth.
$^c$ Number of particles.
$^d$ Rate of particle number growth.
$^e$ a, with VA; b, with BPO; a/b, see the legend to Table I.

## The Radical Concentration in Particles

The average fractional rate per particle, $R_{ppf}$, can be taken as a semiquantitative equivalent of the average number or radicals per particle ($n$). In the range of low conversion the number of radicals per particle strongly decreases with conversion. This can be ascribed to the strong association of the unstable primary particles and the radical desorption. In the medium conversion, the radical concentration in the particles with VA was found to decrease slightly with conversion whereas that with BPO more strongly. The radical concentration in particles with VA is 4 times higher than that with BPO. In both systems the particle diameter and particle number change only slightly with conversion and therefore particle instability or particle association cannot be responsible for the decreases of radical concentration in polymer particles (mainly in the BPO system) (see Table II). The mechanism of the radical formation and termination in the aqueous phase is similar in both systems. Different behavior is expected in the monomer/polymer phase.

The diffusion of BPO molecules (up to 20 wt%) into the monomer/polymer phase promotes the formation .of radicals in this phase. Radicals (derived from the oil-soluble initiator) desorbed from the polymer particles were reported to be very active in the continuous phase termination.[1,2] Thus, the presence of BPO molecules in the polymer particles should favor deactivation by desorption and subsequent reaction with growing radicals in the continuous phase. The very low rate of radical formation in particles, however, due to the low initiator efficiency (the polymerization of macromonomers $f$ was reported to be around 0.2[21]) and decreased decomposition of initiator in the viscous reaction medium[24] disfavor the applicability of the continuous phase initiation and/or termination mechanism[1,2] and/or the generation of radicals in the particles by the "pair radical" mechanism.[25] Under such conditions, the rate of radical formation is lower by approximately 2 orders than that in the continuous phase (see later) and the kinetic efficiency of primary radicals should be very low. The high viscosity of the particle interior favors the cage effect which depresses the generation of primary

radicals.[26-28] The probability of the escape of the radical from the cage in the particle interior and formation of single (remained and desorbed) radicals is very low and under the present conditions (large volume of cage effect, low volume of particle interior and the high concentration of the mobile BPO molecules) theoretically equals zero.[26-28]

The existence of single radicals, however, and their desorption from the particles were proved and discussed in many papers, for example.[1,2,29] The coexistence of growing (entangled) and primary radicals at high conversions with gel effect was reported by Hamielec et al.[30] These findings together with the high number of BPO molecules or the radicals pairs in particle interior led us to suggest a termination mechanism in which the entangled propagating radicals react with the BPO molecules or/and with BPO radical pairs in the volume in which the cage effect is operative. These reactions terminate growing radicals and release simultaneously single (primary and radicals derived from initiator by the chain-transfer process) radicals. The very large half lifetime of the propagating radicals (with the macromonomer active end the half life time was reported to around 50 min at $30°C^{23}$), high concentration and mobility of BPO molecules or the radical pairs favor this reaction. The high mobility and hydrophobicity of primary radicals derived from BPO are supposed to be very active in termination events in the hydrophobic particle core. Although the weight fraction of the mobile radicals is small, the role they can play in termination is important because of their larger diffusion rates (diffusion coefficient of the primary radicals or BPO molecules is about $10^{-7} \, cm^2 \cdot s^{-1}$,[31] and that of the growing (entangled) about $10^{-13} \, cm^2 \cdot s^{-1}$).[30] The strong decrease of the propagation and initiation events already at medium conversion points out the termination reactions are operative in the system.

## Particle Nucleation and Size

The clear reaction system at low conversion indicates that the reaction begins as a homogeneous solution process in which macromolecules with hydrophobic and hydrophilic units (a graft copolymer) are formed. The amphiphilic macromolecules associate with themselves or with monomer or/and precipitate from the medium and from organized structures and later polymer particles. The primary particles or macromolecular clusters are supposed to consist of the hydrophobic core and hydrophilic shell. The graft copolymer (a steric stabilizer) is formed during polymerization and adsorbed on growing particles until there is a sufficient grafted copolymer on the particle surface to stabilize particles against coalescence.[8,17,18]

The rate of primary radical formation, $R$, can give some information about the particle nucleation mechanism. The rates of primary particle formation were estimated to be $2.6 \times 10^{16}$ particles $\cdot dm^{-3} \cdot s^{-1}$ and $5.1 \times 10^{16}$ particles $\cdot dm^{-3} \cdot s^{-1}$ for VA and BPO, respectively, and they agree very well with the experimental values of particle concentration. The stabilizer-free dispersion polymerization (the stabilizer is formed during the polymerization), high rates of primary particle formation and relatively low concentration of stable polymer particles at about 10% conversion propose the strong association of the primary particles at low conversion range (see Table II). In the nucleation period, the association of particles plays a dominant role in polymerization, i.e., particle association regulates the size and number of polymer particles as well as rate of polymerization.[32] Therefore, slight difference in the rates of primary particle formation should not be important. The difference in the initiator distribution is the second factor that strongly influences the reactivity of the polymer particles. The low rate of particle growth in the BPO system favors the formation of a larger number of small particles at low conversions. The stabilizer formed is distributed among a

larger number of small polymer particles and stabilizes them more effectively, resulting in a larger number of small polymer particles. Growing slowly, they capture all newly formed graft copolymer molecules or oligomer radicals with lower molecular weight and hence increase particule stability and concentration. The low radical activity of polymer particles may result from the strong chain-transfer to macromonomer[8,21,23] and desorption of monomeric radicals[28] (these events are the same in both systems) and increased bimolecular termination in the BPO system. The desorption of radicals from polymer particles is known to be inversely proportional to particle size[33] and therefore increased radicals desorption is more expected in smaller particles with BPO.

Huo et al.[34] and Capek[35] found that an inhibitor which is soluble in the oil-phase causes increase in the particle number and deacrease in the rate in the styrene polymerization and acrylonitrile–butyl acrylate copolymerization, respectively. These results shows that depressed propagation in the monomer-swollen micelles or small particles leads to the formation of larger number of polymer particles. Thus, the incorporation of inhibitor molecules into growing chains and/or participation of BPO radical pairs in termination reactions may slow down growth events.

The rates of particle size and number growth obtained by the graphical differentiation of the particle size *versus* time and the number of particles *versus* time data, respectively, are also different. In the system with VA, both rates are nearly constant while with BPO strongly decrease with conversion. Particle size and number data served to estimate the critical number of particles per unit volume and was around $2.5 \times 10^{14}$ per cm$^3$. In the range of low conversion, the number of particles in the BPO system is closer to the critical value and therefore particle nucleation is more depressed. For example, stable polymer particles formed in the BPO system reach the diameter *ca.* of 70 nm at 10% conversion while those with VA

100 nm. At medium conversion, particles in the both systems reach nearly the same diameter. This behavior results from the same amount of the amphiphilic macromonomer incorporated in the copolymer (stabilizer) and critical number of particles reached.

Polymer dispersion with relatively narrow particle size distribution ($D_w/D_n$) throughout polymerization occurs. In the system with VA $D_w/D_n$ is below 1.1 and with BPO, below 1.05. Thus, coalescence between large particles is negligible and therefore a narrow particle size distribution is retained. These results show that the homoassociation of large particles is not important. The higher monodispersity in the BPO systems probably results from the formation of a larger number of stable particles at low conversion. The formation of graft copolymers (a surfactant) during the polymerization, particle nucleation mode and high radical and dead polymer (both formed in the continuous phase) capture efficiency of particles may be responsible for the formation of uniform polymer particles. The decrease of macromonomer amount in the continuous phase with conversion favors the formation of unstable primary particles (a stabilizer with a lower fraction of amphiphilic monomer units and lower concentration is formed[8]) and heteroassociation of stable and unstable particles that suppresses formation of new stable particles.

## The Molecular Weight Parameters

The polymer molecular weights were found to be $7.0 \times 10^4$ and $1.9 \times 10^4$ at 50% conversion for VA and BPO, respectively (Table III). This does not agree with the expectation of the inverse correlation between particle size and molecular weight.[36,37] Thus, in the case of small particles, a higher proportion of particle-phase polymerization should occur because solution-initiated oligomer radicals or primary particles are captured more efficiently by monomer-swollen polymer particles owing to their greater surface area. The experimental data, however,

**Table III.** Variations of the molecular weight parameters in the dispersion copolymerization of styrene and MMA–PEG macromonomer with the type of initiator and conversion

| Conversion | $\bar{M}_n\ (\times 10^4)^a$ | | | $\bar{M}_w/\bar{M}_n^{\ b}$ | | $D_p/dt\ (\times 10^3)^c$ (unit·s$^{-1}$) | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| % | a$^d$ | b$^d$ | a/b$^d$ | a$^d$ | b$^d$ | a$^d$ | b$^d$ | a/b$^d$ |
| 5 | 3.5 | 0.3 | 11.6 | 2.0 | 2.0 | | | |
| 10 | 7.8 | 0.5 | 15.6 | 2.1 | 2.1 | 111.0 | 7.5 | 14.8 |
| 30 | 20.3 | 1.3 | 15.6 | 2.5 | 2.1 | 75.0 | 5.5 | 13.6 |
| 40 | 24.2 | 1.6 | 15.1 | 2.8 | 2.0 | 48.0 | 2.8 | 17.1 |
| 50 | 27.3 | 1.9 | 14.4 | 3.0 | 2.0 | 22.0 | <0.1 | >100 |
| 60 | 29.6 | 1.9 | 15.6 | 3.2 | 2.0 | | | |
| 70 | 31.2 | | | 3.4 | | | | |

[a] The number-average molecular weight.
[b] The molecular weight distribution.
[c] The average rate of the growth of the macromolecule length in the monomer units per s.
[d] a, with VA; b, with BPO; a/b, see the legend to Table I.

showed the opposite to be true.

In both systems the molecular weights increase with conversion and increase is more pronounced in the range of medium conversion. In the low conversion range continuous (homogeneous) polymerization is dominant. The extrapolation of the molecular weights to zero conversion gives nearly the same value for both systems. This finding indicates that the continuous phase (homogeneous) polymerization proceeds under the same reaction conditions. In this range, the formation of low molecular weights is more pronounced in the BPO system. Thus, the graft copolymer formed with BPO should be more rich in macromonomer. Indeed, the relative reactivity of macromonomer $(M_2)$—$(1/r_2)$ has been found to be 0.77 for heterogeneous (in water/ethanol) and around 0.9 for homogeneous (in DMF and benzene) copolymerization.[38] The stabilizer (the graft copolymer formed in the continuous phase) with higher fraction of PEG macromonomer units forms more stable and a higher number of particles.[8]

The increase of the molecular weight with conversion in the dispersion systems can be ascribed to the transfer of radical activity from the homogeneous to the polymer phase. Thus,

at low conversion the polymers are formed in the continuous medium and in small hydrophilic particles. Under such conditions, the termination rate is high and molecular weight low. The formation of large particles with hydrophobic core favors the formation of polymers with high molecular weight due to the depressed termination rate. Molecular weights with VA are about 4 times those with BPO. The difference indicates that the growth of macromolecules is more pronounced in the VA system. Radical formation in continuous phase thus favors more the propagation steps and therefore the generation of polymers with higher molecular weights is observed. The diffusion mass transfer of the initiator to the polymer phase and reaction of primary radicals or BPO pair radicals probably depress strongly propagation events and therefore low molecular weight polymers are formed.

The molecular weight distribution data $(\bar{M}_w/\bar{M}_n)$ in Table III show a little difference with conversion at the beginning of polymerization but a large one at higher conversion. The same values of $\bar{M}_w/\bar{M}_n$ result from the strong contribution of the continuous (homogeneous) phase polymerization. The formation of polymer in particles thus proceeds in different

ways. In the VA system, the particles generate the polymer with higher molecular weight and much broader molecular weight distribution. Thus, the restricted termination of propagating radicals in particles favors growth. In the BPO system, bimolecular termination is supposed to be very operative also in the particle phase that keeps molecular weight and molecular weight distribution close to those in the continuous phase. That the polydispersity index is generally only slightly above 2 is an argument in favor of transfer to initiator or/and reactions with BPO molecules or its radical fragments.[39] The relatively low molecular weights observed may result from chain transfer reactions to monomer, initiator and surfactant (a graft copolymer) and monomolecular deactivation (formation of stable and occluded radicals).[21,23]

The relative rate of macromolecule length growth may be taken as a semiquantitative equivalent of the apparent average life time of propagating radicals (or an inactive period) (Table III). In both systems, the relative life time of propagating radicals thus decreases with conversion and is *ca.* 15 times larger in the VA system. We believe that the accumulation of BPO molecules (or its radicals) in the viscous polymer particle interior increases termination rates between polymeric radical and mobile radicals which decrease the half life time of growing chains. These differences in the apparent life times of growing radicals (or the radical activity) for VA and BPO systems are in good agreement with the parameters (the radical concentration per particle) obtained from kinetic data (Table I).

## CONCLUSIONS

From the foregoing discussion it appears that the formation of radicals in the continuous phase is mainly responsible for the growth and higher radical activity of polymer particles in the VA system. The diffusion of initiator to the monomer/polymer phases increases termina-

tion mainly in polymer particles which decrease both the rate and polymer molecular weight. The large lifetime of growing radicals due to steric hindrance around the active end and high viscosity of the particle interior promote the high deactivation activity of mobile radicals. The results obtained with VA are consistent with the radical entry mechanism for the classical emulsion polymerization initiated by the water-soluble initiator with high contribution of chain-transfer and desorption. The experimental results with BPO are against the dominant role of continuous phase termination. BPO molecules or radical pairs are supposed to react with entangled propagating radicals in a volume in which the cage effect is operative (the heterogeneous cage effect). This reaction terminates growing radicals and simultaneously releases single radicals. The deactivation of particles with BPO molecules is supposed to increase with the particle fraction, hydrophobicity and viscosity of the particle interior. At medium conversion, the polymer particles effectively absorb newly formed oligomer radicals in which deactivation reactions with BPO molecules or radicals take place. Thus, the polymer particle seems to act as a radical scavenger.

Similar behavior was observed in the dispersion copolymerization of benzyl methacrylate with the methacroyl terminated poly(ethylene glycol) initiated by water (VA and potassium peroxodisulfate)- and oil (AIBN)-soluble initiators in water and heptane.[40] The location of the initiator in continuous or monomer droplet phases favored initiation and propagation and high polymerization rates were observed. The distribution of the initiator between continuous (heptane) and monomer/polymer phases led to low polymerization rates.

The results of Asua *et al.*[1,2] are principally consistent with the present mechanism with radical formation in both phases but with dominant continuous phase termination. Even Nomura *et al.*[4,5] reported that polymerization

is governed by the decomposition of the water-soluble fraction of the oil-soluble initiator. Trends of exponents with respect to the concentrations of the reactants seem to support the mechanism of increased radical termination in the polymer phase. The rate of polymerization of styrene was reported to be 0.5 and 0.3 with respect to the emulsifier (above the CMC) and oil-soluble initiator concentrations, respectively. The number of polymer particles was proportional to the exponent 0.7 with respect to the emulsifier concentration. Thus, the number of particles increased more whereas the rate of polymerization was depressed. The depressed growth of polymer particles caused by the radicals derived from the oil-soluble initiator thus promotes the nucleation of the higher number of monomer-swollen emulsifier micelles. The value of 0.3 on [I] obtained in the stationary interval indicates increased radical termination within the particle by mobile radicals.

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