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DISPERSION COPOLYMERIZATION OF POLYOXYETHYLENE MACROMONOMER AND STYRENE—2.* EFFECT OF INITIATOR TYPE AND CONCENTRATION ON THE POLYMERIZATION PROCESS

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Abstract—The dispersion copolymerization of methacryloyl-terminated polyoxyethylene (PEO-MA) macromonomer and styrene initiated by a water/ethanol-soluble (2,2′-azobis(N,N-dimethyleneisobutyramide, VA) and oil-soluble (dibenzoyl peroxide, DBP) initiators was investigated at 60°C. The rate of polymerization and the number of particles were found to increase with increasing concentration of initiator. The initial rate of polymerization was found to be proportional to the 0.6 and 0.8th power of [VA] and [DBP], respectively. The rate per particle was observed to be proportional to the 0.17th and 23rd power of [VA] and [DBP], respectively. In the VA systems the polymerizations were faster and the molecular weights of graft copolymers larger. The dependence of the particle number was described by a curve with a minimum at *ca* 15 or 20% conversion. The partition of DBP molecules between the continuous phase and the polymer particles causes the formation of radicals in both phases. The DBP molecules or DBP radical fragments located in polymer particles take part in both initiation and termination events. The latter is suggested to be responsible for the low rates and molecular weights of graft copolymers.

INTRODUCTION

It has been recognized that macromonomers are very important for the preparation of various kinds of graft copolymers with a different number and length of branch segments [1–4]. With regard to the solution copolymerization of macromonomers (M_1) with conventional small comonomers (M_2), the monomer reactivity ratio (r_2), the copolymer composition and the rate of copolymerization were intensively investigated, e.g. Refs [1–6]. Deviations from ideal copolymerization behaviour are observed due to intramolecular phase separation, diffusion effects, and steric factors. On the copolymerization reactivity of a macromonomer, the following can be considered as major influencing factors: (1) the reactivity of the polymerizable end group associated with its chemical structure; (2) enhanced diffusion controlled polymerization of macromonomer; and (3) the incompatibility of unlike polymer chains.

In the copolymerization of a macromonomer with a small monomer it would be very difficult, if not impossible, to generate copolymerization data reflecting a wide range of compositions because of the larger difference in the molecular weights of the reaction partners. Also at the high molar macromonomer concentrations in the charge, the viscosity of the system would become prohibitively large and the kinetic parameters (the reactivity ratios, the termination rate constant...) would become diffusion controlled. To avoid these negative effects the copolymerization is carried out under conditions, $[M_1] \ll [M_2]$. Under such conditions, for example, the Mayo–Lewis equation [7] holds the form (Jaack's equation [8])

$$r_2 = (\mathrm{d}[M_1]/\mathrm{d}[M_2])/([M_1]/[M_2]). \qquad (1)$$

The reciprocal of r_2 is a measure of the relative reactivity of the macromonomer M_1, compared to a small monomer as a reference, towards a growing radical of a small monomer.

Ito *et al.* [9] have investigated the solution radical copolymerization of methacryloyl-terminated poly(ethylene oxide) macromonomer with styrene. The macromonomer's relative reactivity was found to decrease by a factor as much as about 1/2 ($1/r_2 \propto 1.0$, M_n *ca* 1000). Besides, the relative reactivity of the PEO macromonomer was reported to decrease with increasing molecular weight of macromonomer and the viscosity of the reaction medium [10]. The authors [9, 10] have proposed a repulsive interaction between different polymer chains, a macromonomer and a propagating polymer radical in this case, as a factor responsible for the reduced macromonomer's reactivity.

However, little attention has been paid to the effect of dispersion media on the polymerization and/or copolymerization behaviour [2, 3, 11]. Dispersion polymerization is based on the homogeneous nucleation

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of particles from the reaction medium, in a manner similar to the particle formation in an emulsifier-free emulsion polymerization. The mechanism of dispersion copolymerization of PEO macromonomers is very complex and poorly understood, because the PEO macromonomer itself acts as a monomer as well as a stabilizer.

Amphiphilic PEO macromonomers were found to polymerize or copolymerize in water with an unusually high rate that has not been observed for the solution polymerization of a conventional monomer or macromonomers [4, 12, 13]. The laser light scattering studies of the PEO macromonomers revealed the organization of these macromonomers in the aqueous phase into micelles [12].

Poly(ethylene oxide) macromonomers carrying an n-dodecyl group as the ω-end and a methacryloyl group as the α-end were used as comonomers in emulsion copolymerization with styrene initiated by a water-soluble initiator [14]. The macromonomer's relative reactivity was found to increase by a factor as much as about 2 ($1/r_2 \geqslant 2.0$, for the number of EO 9 or 20). These results were explained by the preferential polymerization on the surface of the micellar particles where the macromonomers are enriched.

In our previous studies [13, 15] we have investigated the kinetics of the homogeneous as well as heterogeneous copolymerization of PEO macromonomers with styrene. In this present study we investigate the effect of the initiator type and concentration on the dispersion copolymerization of PEO macromonomer with styrene. Also, the effect of the initiator blend on the kinetics is investigated. The water-soluble initiator is expected to start the polymerization in the aqueous phase whereas the oil-soluble initiator decomposes in both phases (the continuous phase and the monomer-swollen polymer particles). Understanding the particle formation and the growth events in the presence of VA and/or DBP is the major aim of the experiments described here.

EXPERIMENTAL

Materials

Commercially available styrene (St) monomer and initiators VA-061 [2,2′-azobis(N,N-dimethyleneisobutyramide), water- and ethanol-soluble, VA] and dibenzoyl peroxide (DBP, oil-soluble) were purified by usual methods. Twice-distilled water, ethanol and dimethylformamide were used as a polymerization medium. Methacryloyl terminated polyoxyethylene (PEO-MA, $M_n = 1000$) was supplied by NOF Corp., Ltd.

Polymerization procedure

Batch dispersion copolymerizations of PEO-MA macromonomer and styrene were carried out at 60°C. In all runs the recipe containing 5 ml of ethanol/water (4/1, v/v) or 5 ml DMF, 1.11 g of styrene and 0.3 g of PEO-MA macromonomer was used. Amounts of VA and DBP varied as shown later. The polymerization technique, conversion, particle diameter and copolymer composition (NMR method) determinations, calculations of the number of particles and the cleaning of polymer latexes have been described in detail elsewhere [15–17].

Molecular weights of macromonomers and copolymers were determined by means of a vapour pressure osmometer (Corona Model 117) and by gel-permeation chromatography with a Shimadzu LC-6A system with Shodex column (AC-8034, 8 × 500 mm), calibrated with standard polystyrenes (Polymer Lab., Ltd) and poly(ethylene oxides) [17] (Tokyo Soda Co. Ltd). Dimethylformamide was used as an eluent. The GPC elution pattern of the PEO copolymers obtained showed a single peak.

A light scattering method was used to estimate the weight-average molecular weight at 25°C in CCl_4. Intensities of light scattered by copolymer solutions were measured with a Chromatix KMS-6 in CCl_4 using a vertically polarized primary beam of wavelength 546 nm. Sample solutions were filtered through a membrane of pore size 0.2 μm, Toyo Roshi Co. Ltd.

Refractive index increments (dn/dc) of PSt and PEO-St graft copolymers were determined in CCl_4 with a visual differential refractometer Brice–Phoenix BP-2000-V at 25°C for a wavelength of 546 nm.

The viscosity was measured at 25°C in CCl_4 with an Ubbelohde-type viscometer. Intrinsic viscosities, $[\eta]$, were determined from extrapolation of the plots of the reduced viscosities, η_{sp}/c and $\ln \eta_{rel}/c$, vs the concentration of polymer.

RESULTS

The nature of the polymerization medium

The polymerization begins as a homogeneous solution process in which macromolecules (graft copolymer molecules) are formed. In ethanol/water the amphiphilic macromolecules (macromonomers and/or graft copolymer molecules) associate with each other to form micelles or primary particles [4, 12, 13]. Below *ca* 5% conversion the reaction medium is transparent. As polymerization proceeds (above 5% conversion) the homogeneous system transforms to a heterogeneous (dispersion) one.

Analysis of the reaction mixture

The differences in kinetic, molecular weight and colloidal parameters of the dispersion polymerization may be discussed in terms of the hydrophilic–hydrophobic properties of (macro)monomers, the formation of aggregates and partitioning of (macro)-monomer (or initiator) between the continuous phase and polymer particles.

By mixing styrene, ethanol, water (in the volume ratio 1/4/1) and PEO-MA macromonomer the transparent disperse system was formed. To model partitioning of PEO macromonomer and DBP initiator between the continuous and monomer/polymer phase the mixtures styrene/ethanol/water (5/4/1, v/v/v) and (5/2.5/2.5, v/v/v) were used. The partition coefficient, which was defined as the weight ratio of the PEO-MA amount in styrene to that in the continuous phase, is 0.15 and 0.16, respectively. The observed partition coefficient may favour the formation of the PEO-rich growing radicals with a high solubility in the continuous phase.

The partition coefficient of DBP initiator between the styrene and continuous phase (styrene/ethanol/water = 5/4/1, v/v/v) is 0.25 which is in a good agreement with that (0.27) for the polymer particles/continuous phase [15]. We were unable to obtain the partition coefficient for styrene between the polymer particles and continuous phases.

Rate of polymerization

The conversion–time data for the radical copolymerization of PEO-MA macromonomer with styrene

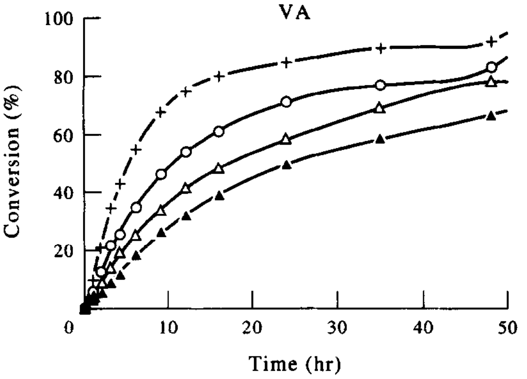

Fig. 1. Variation of monomer conversion in the dispersion copolymerization of PEO-MA macromonomer and styrene with reaction time and initiator (VA) concentration. Contents: 5 ml ethanol/water (4/1, v/v), 1.11 g styrene, 0.3 g PEO-MA, temp. 60°C. [VA] × 10^2/(mol dm^{-3}): 2.18 (+), 1.09 (○), 0.55 (△), and 0.22 (▲).

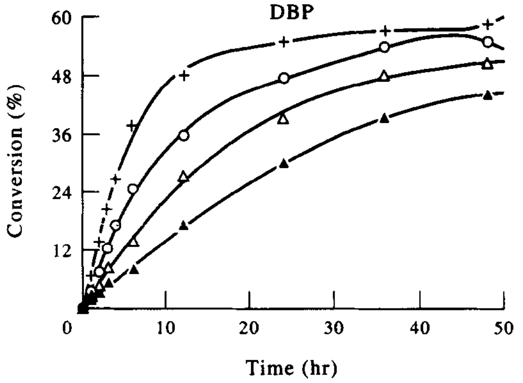

Fig. 2. Variation of monomer conversion in the dispersion copolymerization of PEO-MA macromonomer and styrene with reaction time and initiator (DBP) concentration. Contents: 5 ml ethanol/water (4/1, v/v), 1.11 g styrene, 0.3 g PEO-MA, temp. 60°C. [DBP] × 10^2/(mol dm^{-3}): 2.25 (+), 1.13 (○), 0.56 (△), and 0.23 (▲).

initiated by VA are shown in Fig. 1. The conversion curves were found to be linear up to 10 or the most 15% conversion and then the rate of polymerization gradually decreases up to the total consumption of monomers. In all runs, high conversions are reached. The strong decrease of the rate of polymerization is observed beyond 10 hr. This may be attributed to the consumption of initiator because the half lifetime of VA at 60°C is *ca* 15 hr [18]. After this critical reaction time or conversion the polymerization proceeds under dead-end conditions [19]. In the runs with [VA] $\geqslant$ 1.09×10^{-2} mol dm^{-3} the decrease in R_p results also from the consumption of monomer (high conversion).

The effect of an oil-soluble initiator (dibenzoyl peroxide, DBP) on the radical copolymerization is summarized in Fig. 2. The shape of these conversion curves differs slightly from that of the curves in the Fig. 1. The conversion curves from Fig. 2, however, are linear up to 20 or 30% conversion and reach the limiting conversion at 50 or 60%. This behaviour cannot be attributed to the consumption of DBP initiator or depletion of monomer because the half lifetime of DBP is *ca* 70 hr at 60°C [20] and there is enough free monomer at 50 or 60% conversion.

The rates of initiation for DBP and VA ([VA] = [DBP] = 1.1×10^{-2} mol dm^{-3}) were estimated to be 4.3×10^{-8} mol dm^{-3} sec^{-1} and 2.4×10^{-8} mol dm^{-3} sec^{-1}, respectively (k_d and f taken from Ref. [13]). Thus, the polymerization with DBP should be faster than that with VA. Table 1 shows, however, that the reverse is true. For example, the observed rates of polymerization (R_p) for DBP and VA ([DBP] = [VA] $\sim 1.1 \times 10^{-2}$ mol dm^{-3}) were 3.3×10^{-5} mol dm^{-3} sec^{-1} and 5.1×10^{-5} mol dm^{-3} sec^{-1}, respectively. To explain this behaviour the effect of partitioning of DBP on the initiation rate (in the continuous phase) was followed. The oil-soluble initiator (DBP) partitions between the continuous phase and the monomer swollen micelles or polymer particles. The partition experiments indicate that *ca* 20% of the total DBP initiator is located in the monomer swollen micelles or polymer particles. The rate of initiation estimated

Table 1. Variation of kinetic and colloidal parameters in the dispersion copolymerization of PEO-MA macromonomer and styrene with VA concentration[a]

Run	[VA] × 10^2 (mol dm^{-3})	R_p^* × 10^5 (mol dm^{-3b} sec^{-1})		$R^{\ddagger}_{pp}$ × 10^{21} (mole particle^{-1} sec^{-1c})	D‡ (nm^c)	N§ × 10^{-16} (dm^{-3c})
1	2.18	8.78	5.40	1.13	127	4.8
2	1.09	5.11	2.94	0.87	142	3.4
3	0.55	3.28	1.80	0.64	151	2.8
4	0.22	2.20	1.60	0.60	162	2.3

[a]cf experimental part, [PEO-MA] = 0.06 mol dm^{-3}, [St] = 2.13 mol dm^{-3}. *Rate of polymerization: [b]initial; [c]at 20% conversion. †Rate of polymerization per particle: [c]at 20% conversion. ‡Particle diameter: [c]at 20% conversion. §Number of particles: [c]at 20% conversion.

Table 2. Variation of kinetic and colloidal parameters in the dispersion copolymerization of PEO-MA macromonomer and styrene with DBP concentration[a]

Run	[DBP] × 10^2 (mol dm^{-3b})	R_p × 10^5* (mol dm^{-3c}sec^{-1d})				$R^{\ddagger}_{pp}$ × 10^{22} (mole particle^{-1} sec^{-1c})	D‡ (nm^c)	N§ × 10^{-17} (dm^{-3c})
1	2.25	5.63	2.9	2.70	4.70	2.47	80	1.90
2	1.13	3.26	1.8	1.46	3.26	1.94	89	1.37
3	0.56	1.70	0.8	0.90	1.70	1.59	99	1.00
4	0.23	0.96	0.3	0.66	0.96	1.42	114	0.66

[a]cf. experimental part. *Rate of polymerization; [b]the initial rate of dispersion polymerization (at zero conversion, R_p); [c]the initial rate of homogeneous polymerization (in DMF, R_{ps}); [d]the estimated initial rate of polymerization in the macromonomer/monomer aggregate ($R_{pa} = R_p - R_{ps}$); and [e]the rate of polymerization at 20% conversion (R_{p20}). †Rate of polymerization per particle; [c]at 20% conversion. ‡Particle diameter; [c]at 20% conversion. §Number of particles; [c]at 20% conversion.

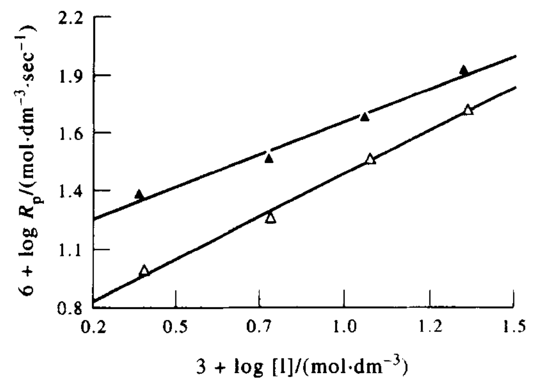

Fig. 3. Variation of the initial rate of polymerization R_p in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and concentration. (▲) VA and (△) DBP. For other conditions see legends to Figs 1 (VA) and 2 (DBP).

from the continuous phase—soluble DBP fraction is *ca* $3.4 \cdot 10^{-8}$ mol dm^{-3} sec^{-1} which is slightly larger than that for the VA system. Thus, the rate of polymerization in both systems should be about the same. The observed difference in R_p, thus, cannot be explained by the solubilization of a certain quantity of DBP which is supposed to be inactive [21].

The initial rates of polymerization determined from Figs 1 and 2 (by a best fitting method) are expressed as a function of conversion and the initiator type and concentration, respectively, in Fig. 3 and Tables 1 and 2. According to the ideal kinetic model (for a homogeneous solution/bulk radical polymerization) [22] and homogeneous nucleation model (for a disperse system) [23], the relation between the rate of polymerization (R_p), the rate per particle (R_{pp}) and the initiator concentration [I] can be expressed as

$$R_p \propto [\mathrm{I}]^{0.5} \quad \text{(a homogeneous polymerization)} \tag{2}$$

or

$$R_p \propto [\mathrm{I}]^{0.4} \; (R_{pp} \propto [\mathrm{I}]^{0}) \quad \text{(a disperse polymerization).} \tag{3}$$

The experimental results listed in Fig. 3 and Tables 1 and 2, however, obey the relationships

$$R_{p,i} \propto [\mathrm{VA}]^{0.6} \text{ or } R_{p,i} \propto [\mathrm{DBP}]^{0.8} \tag{4}$$

and

$$R_{p,20} \propto [\mathrm{VA}]^{0.6} \text{ or } R_{p,20} \propto [\mathrm{DBP}]^{0.7} \tag{5}$$

where the subscripts *i* and 20 denote the initial (close to zero conversion) value and the value at 20% conversion (polymer particles are present), respectively.

The exponents (x) 0.6–0.8 ($R_p \propto [\mathrm{I}]^x$) deviate from both the kinetic models. This behaviour indicates that bimolecular termination between the growing radicals is strongly suppressed in both phases (the continuous phase and the polymer particle interior). Generally, the reaction exponent $x > 0.5$ is attributed to the formation of stable or occluded radicals [24]. Indeed the half life time of the propagating radical ending with the macromonomer unit was reported to be *ca* 50 min (at 30°C) [25]. The formation of stable radicals together with phase separation [26] (growing comonomer radical/macromonomer) favour the first radical-loss process. Bulky substituents (PEO units) around the propagating end increase the lifetime of a radical [25] and suppress the mutual penetration between growing radicals and macromonomer [26]. Besides, the strong chain transfer (degradative) to PEO macromonomer [27] and the multibranched structure of the propagating radicals [28] favour the increase of the exponent x above 0.5.

The rates per particle (R_{pp}) (R_p and N taken at 20% conversion) were found to vary with the initiator concentration. This deviation from the theoretical model may be taken as an indication of the contribution of solution polymerization. To support this hypothesis the copolymerization of St and MMA-PEO macromonomer was carried out in DMF with DBP. The initial rates of the solution polymerization (in DMF, R_{ps}) were found to increase with the DBP concentration (see Table 2, column d). The rate data summarized in Table 2 show that the initial rate of dispersion polymerization (R_p, column b) is higher than that of the homogeneous system (R_{ps}). The difference in the rates is supposed to be caused by the polymerization in organized aggregates (R_{pa}, Table 2, column d). In both systems (solution and dispersion) the rates of initiation were the same. The rate of the rapid (particle) polymerization R_{pa} was estimated from the simple equation using R_p and R_{ps} data

$$R_{pa} = R_p + R_{ps}. \tag{6}$$

This consideration shows that the polymerization proceeds in the aggregates from the start of reaction even when the system is visually transparent.

The effect of a blend of VA and DBP on the dispersion copolymerization of PEO-MA and St was investigated. It was found that the sum of the initial rates ($R_{p,\mathrm{sum}} = 4.9 \times 10^{-5}$ mol dm^{-3} sec^{-1}) for VA (Table 1, run 3, 3.3×10^{-5} mol dm^{-3} sec^{-1}) and DBP (Table 2, run 3, 1.6×10^{-5} mol dm^{-3} sec^{-1}) is larger than the initial rate ($R_{p,\mathrm{blend}} = 3.8 \times 10^{-5}$ mol dm^{-3}) for the initiator blend ([AP] = [DBP] = 5.5×10^{-3} mol dm^{-3}). This finding indicates that the oil-soluble initiator located in the macromonomer/monomer aggregates disfavours the growth events.

The particle and radical parameters

The dependence of the particle size and number on conversion and the type of initiator is summarized in Figs 4 and 5 and Tables 1–4. The size of particles increases abruptly with conversion up to 10 or 15% conversion as a result of the strong association of primary particles (see Fig. 5). At the end of this nucleation period stable polymer particles with critical diameters 120 and 70 nm are formed (for the runs illustrated in Fig. 5). Below 5% conversion the colloidal unstable particles with diameter *ca* 20–30 nm are formed. As polymerization proceeds (above 15% conversion), the particle size grows slightly and the increase is more pronounced with DBP. The diameter of final VA particles is 170 nm (80% conversion) and that of DBP particles 125 nm (64% conversion). Here, the particles size increased approx. 1.4 times from 8 to 80% conversion in the VA run and 1.8 times from 9 to 64% conversion in the DBP run.

Figure 5 shows that the number of particles at first decreases strongly with conversion up to 15 or 20%

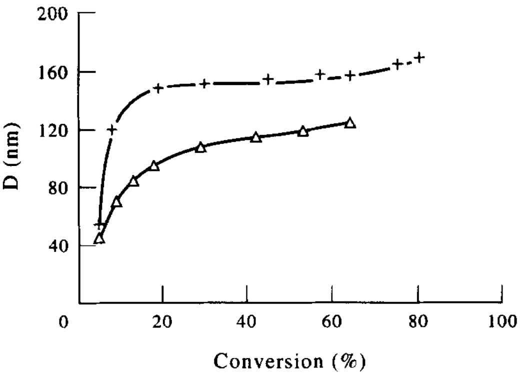

Fig. 4. Variation of the polymer size D in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and conversion. $[VA] = 5.5 \times 10^{-3}$ $mol\,dm^{-3}$ (+) and $[DBP] = 5.6 \times 10^{-3}\,mol\,dm^{-3}$ (△). For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

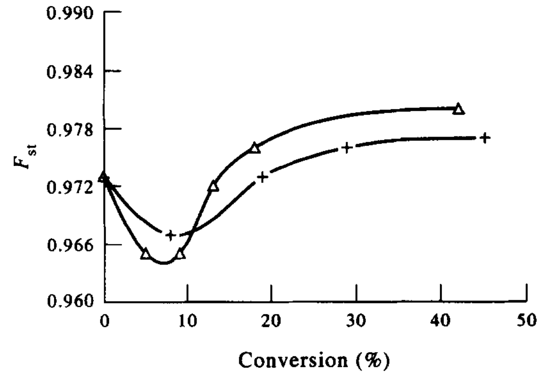

Fig. 6. Variation of the copolymer composition F_{St} (the mole fraction of St) in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and conversion. $[VA] = 5.5 \times 10^{-3}\,mol\,dm^{-3}$ (+) and $[DBP] = 5.6 \times 10^{-3}\,mol\,dm^{-3}$ (△). For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

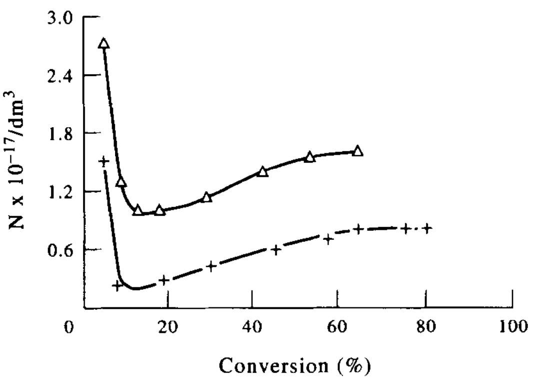

Fig. 5. Variation of the number of polymer particles N in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and conversion. $[VA] = 5.5 \times 10^{-3}\,mol\,dm^{-3}$ (+) and $[DBP] = 5.6 \times 10^{-3}$ $mol\,dm^{-3}$ (△). For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

(reaches a minimum), then slightly increases up to 50 or 60% and finally reaches the plateau value. The DBP system produced smaller and a higher number of particles. The decrease of N with conversion during the nucleation period is caused by the agglomeration of primary particles. In this interval particles grow mostly by association.

The particle size is a function of HLB and concentration of stabilizer. Thus, the ratio of PEO and PSt sequences and the degree of grafting of the PEO/St graft copolymers should govern the particle size (or the properties of a stabilizer—the St/PEO graft copolymer). According to Ref. [29] the molecular weight and the solubility of the graft copolymer (in the continuous phase) are also important. The experimental results indicate that the more efficient stabilizer is formed in the DBP runs (dispersion has a larger number of particles) in which the PEO—richer graft copolymers, thus, should be formed. Variations of copolymer composition with the initiator type and conversion, however, show that the graft copolymer slightly richer in PEO units is formed in the VA runs (Fig. 6). Thus, variations in copolymer composition with initiator type and conversion cannot explain the observed differences in colloidal parameters.

Large differences, however, were observed in the molecular weights of PEO/St graft copolymers. The

Table 3. Variation of final colloidal and molecular weight parameters in the dispersion copolymerization of PEO-MA macromonomer and styrene with VA concentration[a]

Run	$[VA] \times 10^2$ $(mol\,dm^{-3})$	$M^*_{w,LS} \times 10^{-6}$	$DP^\dagger_{w,LS} \times 10^{-4}$	D‡ (nm)	N§ $\times 10^{-17}$ (dm^3)
1	2.18	2.0	1.61	137	1.80
2	1.09	2.1	1.69	156	1.10
3	0.55	4.2	3.39	170	0.80
4	0.22	4.3	3.47	180	0.59

[a] cf. experimental part, 70–90% conversion range. *Weight-average molecular weight (LS). †Degree of polymerization (LS). ‡Final particle diameter. §Final number of particles.

Table 4. Variation of colloidal and molecular weight parameters in the dispersion copolymerization of PEO-MA macromonomer and styrene with BPO concentration[a]

Run	$[BPO] \times 10^2$ $(mol\,dm^{-3})$	$M^*_{w,LS} \times 10^{-5}$	$DP^\dagger \times 10^{-3}$	D‡ (nm)	N§ $\times 10^{-17}$ (dm^{-3})
1	2.25	1.2	1.05	107	2.40
2	1.13	2.0	1.61	112	1.90
3	0.56	2.5	2.02	125	1.60
4	0.23	3.0	2.42	130	1.34

[a] cf. experimental part, 50–60% conversion range. *,†,‡,§See Table 3 legend.

values of M_w were generally by 1 order in the magnitude larger in the VA runs than those in the DBP ones. Besides, light scattering measurements detected two fractions of polymers [the low molecular (LMW) $\sim 10^5$ and high molecular weight (HMW) $\sim 10^6$ polymer fraction] in each sample. The DBP system contains mostly the low molecular weight copolymers (*ca* 95 wt%). On the contrary, the VA system contains the 10 wt% of the low molecular weight graft copolymers and the rest—90 wt%—is the high molecular weight copolymer.

These results indicate that the efficiency of PEO graft copolymer as a stabilizer decreases with its molecular weight. Indeed the large PSt/PEO polymer molecules were reported to associate themselves and to form local micro domains [30]. This type of aggregation may decrease the active fraction of PEO units used to stabilize polymer particles.

Experimental results show that the DBP system contains a higher concentration of particles and therefore larger rates of polymerization should be found. Tables 1 and 2 show that the reverse is true, i.e. the higher rates are observed in the VA systems. To explain this behaviour the dependence of the rate of polymerization per particle on the initiator type was followed.

The rate of polymerization per particle, R_{pp}, can be taken as a semiquantitative equivalent of the average number of radicals per particle ($\bar{n}$). The number of radicals in the VA system is *ca* 10 times as large as that in the BPO system (see Tables 1 and 2). Thus, the DBP saturated monomer/polymer particles are less reactive than those without initiator (VA runs, VA is not located in monomer/polymer particles).

A complex character of the present dispersion copolymerization results from the polymerization in the continuous phase as well as in polymer particles.

The contribution of the homogeneous polymerization may be also evaluated from the following dependences

$$R_{pp,20} \propto [\mathrm{VA}]^{0.17} \text{ and } R_{pp,20} \propto [\mathrm{DBP}]^{0.23}. \qquad (7)$$

The exponents 0.17 and 0.23 show that the homogeneous polymerization is more pronounced in the DBP runs.

The following relationships

$$R_{p,20} \propto N^{1.3} \text{ (for VA) and } R_{p,20} \propto N^{1.5} \text{ (for DBP)} \qquad (8)$$

deviate from the kinetic model and the deviation is more pronounced in the DBP runs. The reaction orders 1.3 and 1.5 indicate that the nucleation of particles increases with the initiator concentration. This finding supports the idea that the surfactant activity of a PEO graft copolymer increases by decreasing the molecular weight of a PEO graft copolymer. The decrease of M_w with increasing initiator concentration is documented later.

Molecular weights and copolymer composition

Variations of the weight—average molecular weights with conversion and the initiator type and concentration, are summarized in Tables 1–4 and Figs 7 and 8. The molecular weights were found to increase with conversion and the increase is more pronounced in the VA systems (especially at low and medium conversion) (Fig. 7). The molecular weights in the DBP system vary only slightly with conversion. The extrapolation of the molecular weights to zero conversion gives nearly the same value for both systems. This finding indicates that the polymerization starts in both systems under the same reaction conditions and/or the same rate of initiation.

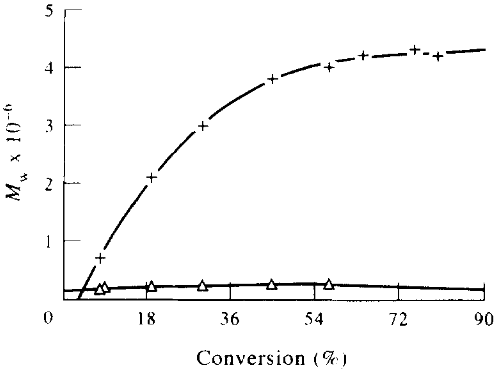

Fig. 7. Variation of the weight-average molecular weight M_w in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and conversion. [VA] = 5.5×10^{-3} mol dm^{-3} (△) and [DBP] = 5.6×10^{-3} mol dm^{-3} (+). For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

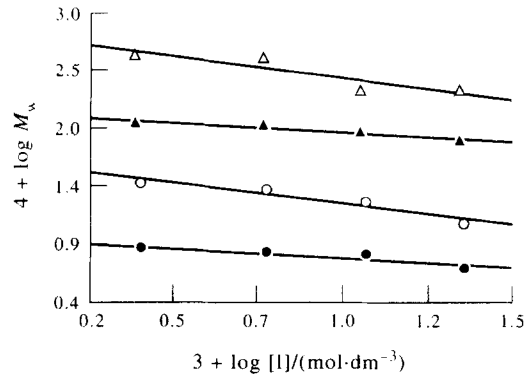

Fig. 8. Variation of the weight-average molecular weight M_w in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and concentration. VA: (△) LS, (▲) GPC and DBP: (○) LS, (●), GPC. For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

The strong increase of the molecular weight with conversion in the VA system results from the transfer of radical activity from the solution to the polymer phase. At low conversion the polymers are mostly formed in the continuous phase in which the termination rate is high and therefore the polymer formed has the low molecular weight. In polymer particles the termination is restricted and therefore the large molecular weight polymers are formed. The experimental data show that the VA systems produced much larger polymers. Thus, the growth of polymer chains in particles is more pronounced in the VA run. The molecular weights in the DBP runs are very similar to those formed in solution copolymerization [13] (the same reaction conditions including [DBP]). These results indicate that the monomer-DBP saturated polymer particle acts as a "homogeneous" reaction locus in which rapid termination dominates.

The molecular weights determined by light scattering (LS) are *ca* three or four times those determined by GPC (Fig. 8). It was reported that the hydrodynamic volume of such highly branched macromolecules (homopolymers) is very small compared with that of linear homologues of the same molecular weight [31, 32]. The measurements of such macromolecules by GPC led to the strong underestimation of M_w [3, 32, 33]. In the case of polymacromonomer the difference between values determined by GPC and LS reached a factor 100. The difference between $M_{w,GPC}$ and $M_{w,LS}$ may be attributed to the underestimation by the GPC method.

The apparent polydispersity index (from GPC data) reaches the values 2.5–3.0 in the VA systems or 1.5–2.0 in the DBP system, respectively. The polydispersity index seems to increase with molecular weight. The generation of polymers in both the continuous phase (*ca* 10 wt% polymer formed) and the polymer particles (*ca* 90 wt% polymer formed) leads to the broader distribution of molecular weights. Besides, the distribution is increased by the chain transfer events.

Molecular weights were found to decrease with increasing initiator (VA or DBP) concentration. The experimental results listed in Fig. 8 and Tables 3 and 4 obey the relationships

$$M_{w,GPC} \propto [VA]^{-0.17} \text{ and } M_{w,LS} \propto [VA]^{-0.38} \quad (9)$$

and

$$M_{w,GPC} \propto [DBP]^{-0.19} \text{ and } M_{w,LS} \propto [DBP]^{-0.37}. \quad (10)$$

The relationships M_w vs [VA] are in a good agreement with those in the kinetic model indicating the restricted bimolecular termination. The branched growing radical can be deactivated by the reaction with a small radical (primary). The difference between exponents 0.17 (or 0.19) and 0.38 (or 0.37) may be taken as an indication of the molecular weight underestimation.

The refractive index increments $(dn/dc)_o$ of PEO graft copolymers were measured to be 0.122–0.128 and 0.144–0.148 for the VA and DBP runs, respectively. The (dn/dc) for PSt and PEO was reported to be *ca* 0.15 (in CCl_4) and 0.04 (in CCl_4) [20]. The $(dn/dc)_c$ of the PSt/PEO copolymer was calculated according to the additive rule

$$(dn/dc)_c = (dn/dc)_{PSt} \cdot x_{PSt} + (dn/dc)_{PEO} \cdot x_{PEO} \quad (11)$$

where x denotes the copolymer composition expressed by weight fraction ($x_{PSt} = 0.79$ and $x_{PEO} = 0.21$), is 0.127. Thus, the (dn/dc) in both systems should be 0.127 because the copolymer composition was the same in all samples used. The experimental results (expecially for DBP runs) however deviate from the value 0.127.

The $(dn/dc)_{PSt}$ of PSt was found to vary with the shape of a polymer coil, e.g. the value 0.15 was reported for a linear polymer, 0.112 for a star shaped polymer and 0.112 for a comb shaped one [20]. These findings indicate that the low $(dn/dc)_o$ for the VA system should be discussed in terms of the formation of the comb shaped PEO graft copolymers.

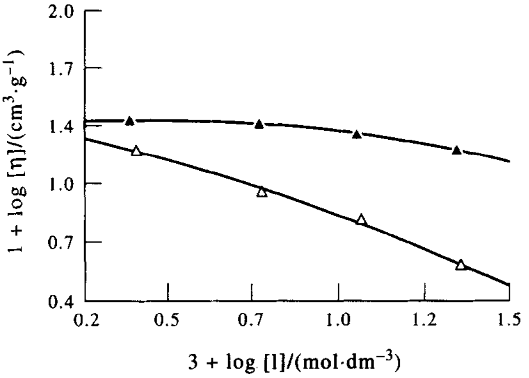

Fig. 9. Variation of the intrinsic viscosity [η] in the dispersion copolymerization of PEO-MA macromonomer and styrene with the initiator type and concentration. VA (▲), DBP (△). For other conditions see the legends to Figs 1 (VA) and 2 (DBP).

The dependence of the intrinsic viscosity [η] of the PEO graft copolymer solutions on the initiator concentration is quite complex (Fig. 9). From this plot one can see that the [η] decreases with increasing initiator concentration and the decrease is very pronounced in the DBP systems. The reason for this finding is the difference in the polymer size, polymer coil density and the polymer–polymer or polymer–solvent interaction. The high molecular weight PEO graft copolymer forms a more closely packed or more compact polymer coil which favours more the polymer–polymer interaction. The mutual influence of PSt and PEO sequences may lead to hydrophobization of the polymer molecules, that is, to weakening of the solvent–polymer interaction. On the contrary the low molecular weight graft copolymer forms slightly packed polymer coils with an intensive interaction polymer–solvent.

The intrinsic viscosities of the PEO graft copolymers are lower than that of the backbone (polystyrene, $M_n = 1.8 \times 10^6$, $[\eta] = 4.1$ in $CHCl_3$ (25°C) and 3.5 in toluene (35°C) [20]). The [η] of the branched PSt ($M_n = 1.8 \times 10^6$) is estimated to be 2.7 (in toluene, 35°C). Thus, the simple branching decreases the size of polymer coil. Besides, the intramolecular interactions and/or segregation of polar and nonpolar segments (in a PEO graft copolymer molecule) can favour and cause local micro separation which decreases the size of a polymer coil. Thus graft copolymers have hydrodynamic volumes and coil sizes smaller than those of the backbones, and therefore elute later than expected from a GPC column and their [η] values are lower.

Variations of the composition of a graft copolymer with conversion, as shown in Fig. 6, indicate that the copolymer composition is enriched in macromonomer units at low conversion. This results from the association of the amphiphilic PEO macromonomers into micelles [12] and their polymerization. The formation of the PEO-slightly richer copolymers in VA systems (the low conversion) results from the higher activity of monomer swollen micelles. The presence of DBP in mocelles seems to depress the growth events. As the polymerization proceeds further, the copolymer is enriched in styrene units. This results from the diffusion of styrene into the particle interior.

The reactivity ratios r_2 [styrene (2)] for the VA and DBP runs were estimated to be 1.2 and 1.3, respectively. Thus, the copolymer formed with VA is slightly more enriched with PEO units. The relative reactivity of PEO macromonomer ($1/r_2$), thus, has been found to be 0.83 and 0.78 for VA and DBP, respectively. The value of $1/r_2$ for the corresponding low molecular weight monomer is reported to be 2.0 [20]. This indicates that the reactivity of macromonomer is much lower than the corresponding small monomer.

CONCLUSIONS

From the foregoing discussion it appears that the graft amphiphilic copolymer (stabilizer) formed in the aqueous phase acts as an efficient stabilizer. This reaction is more pronounced in the DBP runs. The efficiency of PEO graft copolymer was found to decrease with increasing its molecular weight. In the DBP systems a stabilizer with a low molecular weight was formed—this is why the DBP systems contained a higher concentration of polymer particles.

Association of the amphiphilic PEO macromolecules themselves or with graft copolymer molecules increases the local concentration of unsaturated groups as well as the growth events within the organized aggregates.

The VA system resembles classical emulsion polymerization (VA is soluble only in the continuous phase). The VA initiating radicals enter the polymer particles where they initiate the rapid growth events. The hydrophilic VA molecules or their radical fragments do not diffuse into the particle interior.

In the VA runs the formation of primary radicals proceeds only in the continuous phase and the growth events in particles. This is a reason why higher rates and molecular weights were observed in the VA system.

On the contrary the DBP molecules or radical fragments partition between the continuous phase and the monomer/polymer phase. This finding indicates that the radicals are also formed in polymer particles. The presence of the oil-soluble (DBP) molecules or radicals in particles favours termination events. Thus the polymerization in particles is regulated by a rapid radical termination typical for the solution polymerization and/or by a reaction of growing radicals with the DBP molecules or/and with DBP radical pairs in the volume in which the cage effect is operative [15].

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