

Dispersion Copolymerization of Methacryloyl-Poly(ethylene glycol) Macromonomer with Styrene

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Abstract : The methacryloyl terminated poly(ethylene glycol)(PEG-MA) main chain grafted by styrene monomer in copolymerization process was studied. The dispersion copolymerization of (PEG-MA) macromonomer and styrene initiated by a water and oil soluble radical initiator was carried out in ethanol/water mixture at 60°C. The rate of polymerization and number of particles increased with increasing concentration of initiator. On the other hand, the molecular weight of polymer decreased with increasing concentration of initiator and decrease was more pronounced with the oil soluble initiator. The experimental data indicate that the continuous phase soluble initiator favours growth events in particles while the oil soluble termination.

Abstrak : Metakrililol tertambat poli(etilena glikol)(PEG-MA) rantai utama tergraf oleh stirena dalam proses pengkopolimeran telah dikaji. Penyerakan pengkopolimeran (PEG-MA) makromonomer dan stirena termula dengan satu pemula radikal air dan minyak boleh larut di dalam campuran etanol/air pada suhu 60°C. Kadar pempolimeran dan bilangan zarah telah meningkat dengan penambahan kepekatan pemula. Sebaliknya, berat molikul polimer berkurangan dengan peningkatan kepekatan pemula dan berkurangan lebih tampak dengan pemula minyak boleh larut. Data kajian menunjukkan fasa selanjur pemula boleh larut mengesahkan kejadian pertumbuhan dalam zarah sementara pertumbuhan dalam minyak boleh larut terhenti.

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Introduction

It has been recognized that the polymerization of macromonomers is connected with the diffusion and chemical controlled kinetic events. The high segment density, the chain dimensions of macromonomers and/or their coils and polymer chain entanglements differ from those of linear polymer chains. The addition of low molecular weight comonomer is expected to decrease the effect of high segment density and the chain dimensions of macromonomer on the polymerization of macromonomers. When dealing with the polymerization mechanism of macromonomers, a copolymerization system containing the low molecular weight comonomer could be more suitable to follow gradually perturbation in the macromonomer system. The emulsion or dispersion copolymerization which is very closely related to the monomer composition in the reaction loci can give useful information which a homopolymerization cannot provide.

The kinetics of emulsion polymerization of conventional unsaturated monomers that use a water and oil-soluble initiators give to much controversy because contrary to what it would be expected. It is accepted that a soluble fraction of initiator in continuous phase and/or desorbed radical from particles initiated the growth polymer chains (1-3).

Our previous paper dealing with kinetics of dispersion copolymerization of macromonomers indicated that the distribution of an oil soluble initiator between the continuous phase and the

polymer particles strongly influences the growth events and the overall polymerization process (4).

This paper reports on the preparation of polymer dispersion and the influence of the initiator type and concentration on the kinetic and molecular weight parameters of dispersion copolymerization of (PEG-MA) macromonomer with styrene using a water and oil soluble radical initiator in the ethanol/water mixture.

Experimental

Materials

Commercially available styrene (St) monomer was purified by distillation under reduced pressure in a nitrogen atmosphere prior to use. Methacryloyl terminated poly(ethylene glycol) macromonomer (PEG-MA, $M_n = 1000$) was supplied by Nippon Oil and Fats Co. Initiator VA-061 (2,2'-azobis[2-(2-imidazolin-2-yl)-propane], water soluble initiator and BPO (dibenzoyl peroxide), the oil soluble initiator were used without further purification. All solvents were purified in the usual way prior to use.

Copolymerizations

The macromonomer, styrene, and VA or BPO were weighted into a vessel together with 5 ml of ethanol/water (4/1, v/v) and sealed under vacuum after degassing. Copolymerization was carried out for 48 h at 60°C under shaking at 200 rpm in an incubator to control the temperature. In all runs the

recipe containing 1.11 g styrene, 0.3 g PEG-MA macromonomer. Amounts of VA and BPO varied as shown later. The copolymerization technique was adopted from our previous study (5).

Characterization Method

The resulting polymers were first dialyzed in water using a cellulose dialysis tubing to remove unreacted macromonomer, and then the polymers were dried by freeze drying. The polymer conversion of macromonomers was determined by a conventional gravimetry method. The number average molecular weights (M_n) of the copolymer were determined by gel permeation chromatography (GPC) with a Shimadzu LC-6A system with a shodex column AC-800P, calibrated with polystyrene standards. Particle size measurements were achieved by direct observation with a scanning electron microscopy (SEM).

Results and Discussion

The polymerization begins as a homogeneous solution process in which macromolecules with hydrophobic and hydrophilic units (graft copolymer molecules) are formed. In ethanol/water mixture the amphiphilic macromolecules (macromonomers and/or graft copolymers molecules) associate with each other to form micelles or primary particles (4). Below 5 wt% conversion the reaction medium is transparent. As polymerization proceeds the homogeneous system transforms to a heterogeneous

(dispersion) one.

The conversion-time data for the radical copolymerization of PEO-MA macromonomer with styrene initiated by VA are shown in Figure 1. Fig. 1 shows that the linearity of the conversion curve slightly increases with conversion. For example, at $[VA] = 2.2 \times 10^{-3} \text{ mole.dm}^{-3}$ the conversion curve in linear up to 20 wt% conversion and $[VA] = 2.2 \times 10^{-2} \text{ mole dm}^{-3}$ the linearity increases up to 40 wt% conversion and then levels off. Thus, the steady state interval increases with increasing the concentration of initiator. At run with high rates the high final conversion is reached. Thus, the strong decrease in the rate of polymerization after 10 hours in all runs can be ascribed to the depletion of larger part of initiator. After the critical time due to the consumption of larger part of initiator the polymerization proceeds under dead-end conditions (the half time is about 11 hours (6)). With highest VA concentration the strong decrease in the rate of polymerization may also result from the consumption of monomer at which polymerization proceeds under monomer-starved conditions.

Besides the partitioning of monomer between the continuous phase and the polymer particles is very important. It differs from that in emulsion systems in which the particles and monomer droplets coexist. In emulsion system over interval 2 (the stationary interval) the rate of polymerization is constant or can increase due to the gel effect (7). In the emulsion system the continuous phase does not compete with

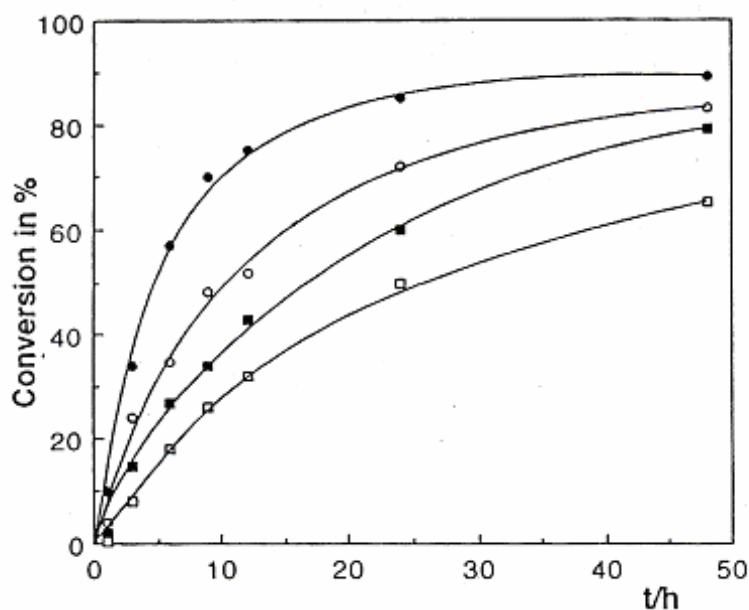


Figure 1 : Variation of monomer conversion in the dispersion copolymerization of PEO-MA macromonomer and styrene, with reaction time and initiator (VA) concentration.

Recipe: 5 ml ethanol/water (4:1, v/v), 1.11 g styrene, 0.3g PEO-MA, temp. 60°C $[VA]$, $10^{-2}/(\text{mol.dm}^{-3})$: 2.18 (●), 1.09 (○), 0.55 (■), 0.22 (□)

polymer particles and/or monomer droplets for a monomer (if they are enough small) dominates. In the percent dispersion system, the continuous phase acts as a monomer reservoir and the reaction medium and competes for a monomer which decreases the monomer amount in particles and the gel effect.

The effect of an oil-soluble initiator (BPO) on the radical copolymerization is summarized in Figure 2.

The shape of these conversion curves is similar to that with VA. They differ from those with VA in the values of final conversions. Here the limiting conversion at 50 or 60 wt% conversion is reached. This behavior cannot be ascribed to the depletion of BPO initiator or monomer because the half lifetime of BPO is about 70 hours at 60°C (8) and there is enough of free monomer at 50 wt% conversion. These results show that the presence of initiator in particles depresses the growth events.

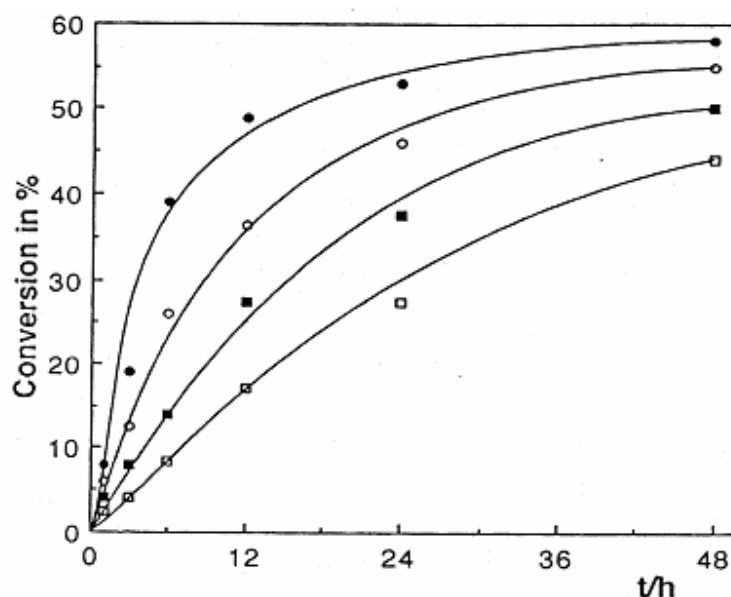


Figure 2 : Variation of monomer conversion in the dispersion copolymerization of PEO-MA macromonomer and styrene, with reaction time and initiator (BPO) concentration.

Recipe: 5 ml ethanol/water (4:1,v/v), 1.11g styrene, 0.3g PEO-MA, temp. 60°C [BPO], $10^2/(\text{mol} \cdot \text{dm}^{-3})$: 2.25 (●), 1.13 (○), 0,56 (■), 0,23 (□). Other conditions are given in the legend to Fig. 1.

Table 1 : Variation of Kinetic and Colloidal Parameters in the Dispersion Copolymerization of PEG - MA Macromonomer and styrene with VA Concentration ^{a)}

$[\text{VA}] \times 10^2$ $\text{mol} \cdot \text{dm}^{-3}$	$R_p \times 10^5$ ¹⁾ $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$	$R_{pp} \times 10^{22}$ ²⁾ $\text{mol} \cdot \text{particle}^{-1} \cdot \text{s}^{-1}$	D ³⁾ nm	$N \times 10^{-17}$ ⁴⁾ $/\text{dm}^3$
2.18	10.4	2.12	127	4.9
1.09	6.65	2.53	156	2.63
0.55	4.0	1.9	168	2.1
0.22	2.7	1.6	180	1.72

a) $[\text{St}] = 2.22 \text{ mol} \cdot \text{dm}^{-3}$, $[\text{PEO-MA}] = 0.05 \text{ mol} \cdot \text{dm}^{-3}$, in ethanol/water (4/1,v/v), 60 °C.

- 1) The maximum rate of polymerization,
- 2) The rate of polymerization per particle,
- 3) Particle diameter,
- 4) Number of particles

Table 2 : Variation of Kinetic and Colloidal Parameters in the Dispersion Copolymerization of PEG - MA Macromonomer and Styrene with BPO Concentration ^{a)}

[BPO] x 10 ² mol.dm ⁻³	R _p x 10 ^{5 1)} Mol.dm ⁻³ .s ⁻¹	R _{pp} x 10 ^{22 2)} mol.particle ⁻¹ .s ⁻¹	D ³⁾ nm	N x 10 ^{-17 4)} /dm ³
2.25	4.8	1.0	107	4.7
1.13	3.1	0.8	112	3.9
0.56	1.8	0.58	117	3.1
0.23	0.9	0.36	120	2.5

a) [St] = 2.22 mol.dm⁻³, [PEO-MA] = 0.05 mol.dm⁻³, in ethanol/water (4/1,v/v), 60 °C.

1-4) See legend to Table 1.

The rates of polymerization (R_p) determined at given conversions (from Fig. 1 and Fig.2) are expressed as a function of the initiator concentration in Table 1 and Table 2. These results show that the rate of polymerization in both initiators decrease with decreasing concentration of initiator. The rate of polymerization per particle (R_{pp}) can be taken as a semi quantitative equivalent of the average number of radicals per particle (N). At low initiator concentration in the VA system the rate of polymerization per particle is 4 times as large as that in the BPO system (see Table 1 and 2). With increasing concentration the difference slows down, e.g., at the highest initiator concentration the rate of polymerization per particle in VA runs is 2 times that in the BPO runs. This behavior favors the deactivation role of BPO molecules in polymer particles.

One of the common arguments to infer a nucleation and polymerization mechanism in particles is the dependence of the rate of polymerization and/or the rate of polymerization per particle on the particle concentration. According to the micellar theory the relation between both parameters can be expressed as

$$R_p \approx N^{0.1} \text{ or } R_{pp} \approx N^0 \quad (1)$$

The values of the reaction order obtained from variation of R_p or R_{pp} with the number of particles by the least-squares method follow the relationships.

$$R_p \approx N^{2.3} \text{ or } R_{pp} \approx N^{0.55} \quad (\text{for VA}) \quad (2)$$

$$R_p \approx N^{2.1} \text{ or } R_{pp} \approx N^{0.7} \quad (\text{for BPO}) \quad (3)$$

In both systems the rate of polymerization increases with the particle concentration in a similar way. The increase is much stronger compared to that supposed by the micellar model (9). This deviation probably results from the formation of amphiphilic copolymers and nucleation of particles throughout the polymerization.

Variation of the number average molecular weights with initiator concentrations are summarized

in Tables 3. Note that the molecular weights with VA are nearly by 1 order higher than those with BPO. The difference indicates that the growth of polymer chains in particles is more pronounced with VA. Thus, the decomposition of initiator and the formation of oligomer radicals in the continuous phase and the entry of oligomer radicals to polymer particles initiated the growth events. The presence of initiator and/or higher radical concentrations in particles depressed the growth of macro radicals and the molecular weights.

The polydispersity index is larger in runs with VA. The generation of polymers in both the continuous phase (small polymers) and polymer particles (large polymers) leads to the broader distribution (between 4 and 6). The molecular weight distribution with BPO is narrower (around 2) which can be ascribed to the dominant polymerization in continuous phase and the chain transfer events.

Molecular weights were found to decrease with increasing initiator concentration and the decrease is more pronounced in the VA system (see Table 3). These can be reasonably explained that with increasing concentration of initiator the formation of radicals in the continuous phase and the entry radical to polymer particles initiated the growth event. The presence of higher radical concentration in particles depressed the growth of macro radicals. Therefore smaller particles are formed. The slight decrease of the molecular weight with BPO concentration result from the slight contribution of latex particles and the dominant role of the chain transfer events in the continuous phase. The strong chain transfer to monomer counteracts that of the initiator concentration and therefore the reaction order x" (from the dependence Mn - (I)^{x"} is very low (≈ 0.1). The polymerization in particles in which termination is regulated by the chain transfer events or bimolecular termination of entangled radicals with mobile radicals leads to the higher reaction order x" = 0.4 (10).

Table 3 : Variation of Molecular Weight Parameters in the Dispersion Copolymerization of PEO - MA Macromonomer and Styrene with VA and BPO Concentration ^{a)}

[VA] x 10 ² mol.dm ⁻³	M _n ¹⁾ (10 ⁵)	M _w /M _n ²⁾	[BPO] x 10 ² mol.dm ⁻³	M _n ¹⁾ (10 ⁴)	M _w /M _n ²⁾
2.18	3.12	3.4	2.25	1.9	2.0
1.09	4.31	3.6	1.13	2.0	1.9
0.55	5.20	3.6	0.56	2.1	1.9
0.22	5.92	5.7	0.23	2.3	1.8

a) See legend to table 2 and 3.

1) The number-average molecular weights,

2) The molecular weight distribution

Conclusions

From the foregoing discussion it appears that the copolymerization of macromonomer with styrene forms the graft amphiphilic copolymer (stabilizer). Association of amphiphilic copolymers from the micelles or primary particles. The rates of polymerization and the molecular weights were larger with VA than with BPO. The continuous diffusion of an oil-soluble initiator (BPO) to polymer particles during the polymerization and its participation in termination suppresses the growth events. The initiator molecules or their radical pairs react with the growing (entangled) radicals in volume in which the cage effect is operative. The reaction diffusion seems to regulate termination of entangled radicals and partly propagation of high molecular weight PEG macromonomers. The mobility of BPO molecules is not restricted at very high conversion. Even under such conditions BPO molecules or its radical pairs may take part in termination events.

The low concentration of mobile radicals derived from VA initiator in particles favors the growth events and increase of the rate and the molecular weight.

The result indicates that the continuous-phase soluble VA favors growth events in particles while the presence of oil-soluble (BPO) molecules or radicals in particles favors termination event.

The chain-transfer to monomer or

macromonomer suppresses the formation of large polymer with the molecular weight distribution around 2. The formation of polymers in the continuous phase and polymer particles is responsible for the distribution parameter much above 2.

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