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The Dispersion Polymerization of Unsaturated Monomers Initiated by the Macromonomeric Initiator

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Summary: The dispersion polymerizations of styrene (St) and methyl methacrylate (MMA) initiated by poly(oxyethylene) macroinimer (PEO-MIM) in ethanol/water were investigated at 50, 60 and 80 °C. The polymerisation rate vs. conversion dependence was described by with a maxim at the beginning of polymerisation. Polymerization was faster with MMA than with St. The limiting conversion was inversely proportional to temperature and was much more pronounced with St. The rate of polymerization increased with temperature. The overall initial activation energy increased with conversion and reached value ca. 25 $kJ.mol^{-1}$ for MMA and 50 $kJ.mol^{-1}$ for styrene at ca. 60% conversion. The particle size was observed to decrease with increasing the macroinimer concentration. The polymer dispersions were unstable and a large amount of coagulum appeared during the polymerisation especially in the styrene-containing reaction system.

Introduction

It has been recognized that macromonomers and macroinimers are very important and widely used for the synthesis of various kinds of functional graft copolymers and special polymer dispersions [1,2]. The ability of macromonomers (macroinimers) to get involved in a copolymerisation is controlled by the reactivity ratios of comonomers, the molecular weight of macromonomers and the type of reaction media. When the macromonomer (macroinimer) or/and graft copolymers formed during the polymerisation are surface active, its polymerisation in the polar media is unusually rapid as a result of its organization into micelles (or organized aggregates). The high segment density at the reaction loci, the polymer chain entanglements, the phase separation of polymer product, etc. influence by a complex way the growth and termination events. In many cases, the heterogeneous nature of these reactions makes the polymerisation reaction mechanism very complex. A special feature of these macromonomers (macroinimers) is the incorporation of hydrophilic and the initiator groups into the polymer matrix.

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The hydrophilic part of macroinimers (macromonomers) is used to be polyethylenoxide (PEO). PEO is a component of a large number of technical products known as stabilizers for polymer dispersions. It is characterized with unusual solution behavior and outstanding properties in the aqueous phase and vailable in wide various variety (molecular weights, copolymer compositions, end groups, etc.) The PEO macroinimer in the (co)polymerisation acts as (co)monomer, stabilizer and initiator as well. PEO-type macroinimers impart the stability of colloidal polymer particles. The hydrophilic PEO-type macroinimers can be used to prepare surface active graft and block copolymers and sterically stabilized polymer dispersions. Macroazoinitiators can thermally homopolymerize by themselves or copolymerize with a vinyl monomer. In each case, the polymerisation leads to the formation of cross-linked polymers.

The objectives of this contribution are report on the application of macroinimer in the radical polymerisation of unsaturated monomers in disperse systems. Macroinimers can be prepared from polyazoester with methacryloyl chloride or 4-vinylbenzoyl chloride 3). Styrene and methyl methacrylate have been chosen as monomers to study the influence the polarity and reactivity on the properties of resulting latex products. Furthermore, the kinetic and colloidal parameters of dispersion copolymerization of PEO macroinimer (PEO-MIM) with MMA or styrene as a function of temperature and macroinimer concentration were evaluated.

Experimental

Materials. Commercially available styrene (St) and methyl methacrylate (MMA) (supplied by Fluka AG) were purified by usual methods. Analytical grade poly(oxyethylene) macroinimer (PEO-MIM, $M_{n,PEO} = 400$, $M^{`}_{n,PEO\text{-}MIM} = 1100$ g/mol) was used. Analytical grade PEO, 4,4'-dicyano-4,4'-azovaleric acid and 4-vinylbenzyl chloride (all supplied by Fluka AG) were used to synthesize PEO-MIM macroinimer according to the procedure, described earlier 4). Twice - distilled water and ethanol were used as a polymerization medium.

Recipe and Procedures. Batch dispersion polymerizations of MMA or St were carried out at 50, 60 and 80 °C. In all runs the recipe contains 1 g monomer, 0.5 g PEO-MIM and 5 ml of a continuous phase (ethanol/water, 4/1, v/v). The polymerization technique, conversion determinations, the particle size measurements and particle number estimations were the same as described in 4-6).

Results and Discussion

Conversion versus time date of the dispersion polymerization of MMA and St initiated with PEO-MIM at different temperatures (50 to 80 °C) are listed in Figs. 1 and 2. The amounts of monomer (St or MMA) and macroinimer are kept constant. The conversion curves are mostly concave downward early on without any a short linear portion. The copolymerisation of PEO-MIM with St reaches the limiting conversion ca at 50 - 80% conversion. The limiting conversion (ca. 80 %) appears also in the MMA/PEO-MIM polymerisation system at the lowest temperature 50 °C. The limiting conversion is inversely proportional to temperature. This behavior can be discussed in following terms: 1) The glassy state. This is reached earlier (at lower conversion) in the runs with lower polymerisation temperature (T_g for PMMA and PSt (ca. 100 °C)) [7], 2) The colloidal stability of polymerisation system. The particle flocculation increased with conversion and the amount of coagulum was much more larger in

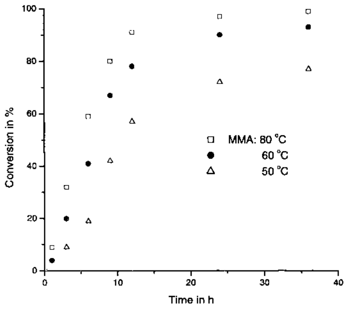

Fig. 1. Variation of monomer conversion with the reaction time and temperature in the dispersion polymerization of MMA and PEO-MIM. Recipe: 1 g MMA, 0.5 g PEO-MIM and 5 ml of a continuous phase (ethanol/water, 4/1, v/v).

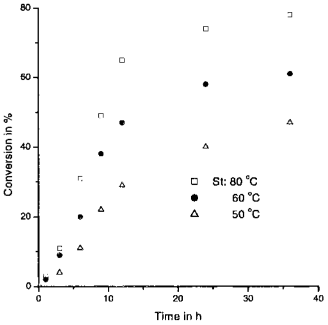

Fig. 2. Variation of monomer conversion with the reaction time and temperature in the dispersion polymerization of St and PEO-MIM. Recipe: 1 g St, 0.5 g PEO-MIM and 5 ml of a continuous phase (ethanol/water, 4/1, v/v).

the St system (up to 30 wt.%). The limiting conversion can be attributed to the phase separation due to which macroinimer and monomer accumulate in the coagulum. The low stability of prepared polymer particles probably results from the low interfacial tension between the PEO-MIM saturated continuous phase and the polymer particles. Under such condition, the driving force to stabilize the polymer particles is lost 8). 3) The consumption of macroazoinitiator. The low half lifetime of initiator and a long polymerisation time can lead to slow polymerisation at longer polymerisation time. The half lifetime of AIBN is ca. 70 h at 60 °C and so the polymerisations at 50 °C and 60 °C can not be influenced by the stronger consumption of macroinitiator 7). The consumption of initiator can be operative in the polymerisation carried out at 80 °C.

Variations of the rate of dispersion polymerization of MMA and St are illustrated in Figs. 3 and 4. The copolymerisation of PEO-MIM is faster with a more reactive MMA monomer than with St ($k_{p,MMA} > k_{p,St}$). The polymerization rate versus conversion curves show a continuous decrease of the rate with conversion The initial rate is the maximal polymerisation rate. At the beginning of polymerisation, the copolymerisation proceeds at a rate similar to a corresponding solution polymerisation 9). After the transformation of transparent medium into the milky one the rate of polymerisation abruptly increased to the maximum. As soon as the large particles accumulated the rate of polymerisation started to decrease. This can be discussed in the following way. The weight fraction of polymer gel increased with increasing amount of PEO-MIM in the reaction mixture but the degree of swelling decreased 4,10). The onset of gel formation starts when the amount of macroinimer is above 5 wt.%. The gel fraction increases with increasing polymerisation time, but the swelling degree of the gel diminishes with time. In the presence of 50 wt.% of PEO-MIM the polymer containing reaction system transforms to the gel. This means that the polymer particles formed during the dispersion copolymerisation of St or MMA with PEO-MIM (50 wt.%) are strongly crosslinked with the very low degree of swelling. Under such condition the polymerisation takes place in the continuous phase and at the particle surface (particle shell). Unsaturated groups at the particle surface initiate the interparticle propagation (agglomeration), the formation of large particles (coagulum) and the immobilization of reactants within the coagulum.

The rate of polymerisation (%conv./h) of the bulk copolymerisation of St with PEO-MIM (34 wt. %) was 32. The rate of dispersion polymerisation of St and PEO-MIM (50 wt. %) was 3. These data indicates that the homogeneous (or precipitation) polymerisation is much faster that the dispersion one. The reverse is true for the conventional homogeneous and dispersion polymerisations [11,12]. The organization of PEO-MIM (graft and block copolymers) in the polar medium probably decreases the homogeneous distribution or diffusion of macroinitiator within the reaction system and so the rate of initiation. This is not the case in the bulk polymerisation (apolar continuous medium) where the macroinimer is homogeneously distributed within the reaction system.

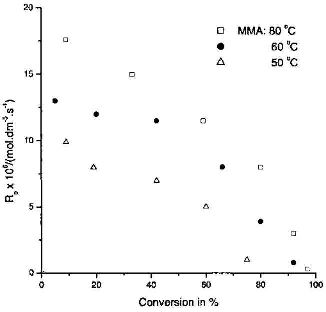

Fig. 3. Variation of the rate of polymerization with conversion and temperature in the dispersion polymerization of MMA and PEO-MIM. Other conditions see in the legend to Fig. 1.

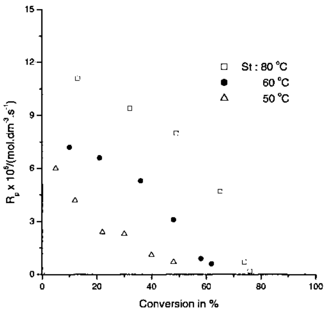

Fig. 4. Variation of the rate of polymerization with conversion and temperasture in the dispersion polymerization of St and PEO-MIM. Other conditions see in the legend to Fig. 2.

Based on the monomer partitioning study [13] and the formation of crosslinked polymer particles, the majority of the monomer (styrene, MMA, and macroinimer) resides in the continuous phase. The polymerization starts in the continuous phase as a solution polymerization. The continuous generation of polymer particles leads to the transfer of reaction loci from the continuous phase to the polymer particles. The result is the reduced bimolecular termination and so the increased polymerisation rate. The polymer product was insoluble in common solvents (toluene, benzene, acetone, THF, dimethylformamide, etc.). This indicates that polymerisation proceeds at the particle surface or particle shell at most.

The overall activation energy of emulsion polymerization ($E_{o,emul}$) and solution ($E_{o,sol}$) can be expressed as follows [14,15]:

$$E_{o,emul} = 0.6\ E_p + 0.4\ E_d \tag{1}$$

$$E_{o,sol} = E_p - 0.5\ E_t + 0.5\ E_d \tag{2}$$

where E_p is the activation energy for propagation, E_t is the activation energy for termination, and E_d is the activation energy for decomposition of initiator. The overall activation energy is estimated to be 80-100 kJ mol^{-1} for solution or bulk polymerization and 50-70 kJ mol^{-1} for emulsion polymerization, respectively [7]. The overall activation for the dispersion polymerisation ($E_{o,disp}$) of PEO-MIM and MMA or St was estimated from the polymerisation rates at Figs. 3 and 4. $E_{o,disp}$ varied with the monomer type and conversion as follows:

$E_{o,disp,MMA}$(kJ.mol^{-1})/%conv.: 20/10, 21/30, and 25/60 (for MMA) (3)

$E_{o,disp.St}$(kJ.mol^{-1})/%conv.: 32/10, 46/30, and 52/50 (for St) (4)

The small $E_{o,disp}$ supports more the dispersion (heterophase) polymerisation or the polymerisation with the low activation energy for initiation. The initiation consists of two processes: 1) the decomposition of initiator and the entry of radicals the polymer particles. The low activation energy can result from the copolymerisation that accumulates the initiator (radicals) in the polymer particles. Furthermore, the overall activation energy increases with conversion and the increase is more pronounced with St. The low activation energy for MMA can be also attributed to the decreased barrier for entering radicals into the polymer particles with increasing temperature [16]. The increased contribution of solution polymerisation might increase E_o in the St system.

The size of polymer particles decreased with the macroinimer concentration and the decrease was more pronounced with MMA than with St (Table 1). Besides, PMMA particles are smaller than PSt ones. PEO acts as a more efficient stabilizer for PMMA particles than for PSt ones. PSt is less polar and has a higher interfacial tension to water than PMMA [17]: $\gamma_{PSt,water}$ = 32.7 mN/m, $\gamma_{PMMA,water}$ = 26 mN/m and water has a much larger surface tension than ethanol (γ_{water} = 72.8 mN/m and $\gamma_{ethyl\ ether}$ = 11.9 mN/m) [18]. It is expected that the interfacial tension PMMA-water/ethanol or PSt-water/ethanol will be smaller than 26 mN/m or 32.7 mN/m. Under such conditions the driving force to stabilize the polymer particles is strongly depressed and so the particle flocculation occurs.

Table 1. Variations of the particle size and particle number with the macroinimer concentration and monomer type.[a)]

[PEO-MIM] ($mol.dm^{-3}$)	D (nm) b)	D (nm) c)	$N.10^{16}$ $/dm^3$ b)	$N.10^{16}$ $/dm^3$ c)
0.0138	340	4100	1.0	0.0001
0.0413	430	620	0.5	0.13
0.069	300	490	1.7	0.28
0.0966	290	530	2.0	0.24
0.138	280	520	2.3	0.27

a) Recipe: 1 g St, 0.5 g PEO-MIM and 5 ml of ethanol/water (4/1, v/v), time = 24 h, temp. 60 °C.

The particle flocculation was more operative at [PEO-MIN] ≤ 0.0413 $mol.dm^{-3}$. The number of polymer particles increased with increasing macroinimer concentration in the MMA polymerization system but did not varied in the St system ([PEO-MIN] > 0.0413 $mol.dm^{-3}$):

$$N_{p,MMA} \propto [\text{PEO-MIM}]^{0.46}$$

Conclusion

The dispersion polymerizations of styrene (St) and methyl methacrylate (MMA) initiated by poly(oxyethylene) macroinimer (PEO-MIM) in ethanol/water formed unstable polymer dispersions. The initial polymerisation rate was the maximum one. The polymerisation rate decreased with increasing conversion and the decrease was more pronounced at high conversion. The limiting conversion was inversely proportional to temperature and the rate at high conversion was much more restricted in the St containing system. The overall activation energy increased with conversion and reached value ca. 25 $kJ.mol^{-1}$ for MMA and 50 $kJ.mol^{-1}$ for styrene at 60% conversion. The particle number increased with increasing PEO-MIM concentration with MMA and was independent of PEO-MIM concentration with St.

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