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MECHANISM OF PARTICLE FORMATION AND KINETICS OF THE DISPERSION POLYMERIZATION OF CYCLIC ESTERS

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Abstract: Pseudoanionic and anionic polymerizations of ε-caprolactone and lactides in 1,4-dioxane:heptane mixtures containing poly(dodecyl acrylate)-g-poly(ε-caprolactone) yield polyesters in form of microspheres. Monitoring partition of active centers between solution and microspheres revealed that particles are formed during initial period, when macromolecules reach their critical masses (ca. 1 000) and became insoluble. Then, propagation proceeds inside of microspheres into which monomer diffuses from solution. Monitoring of variation of the number of particles in a unit volume of reaction mixture with time indicated that after a primary nucleation the delayed nucleation and aggregation are absent. In effect, microspheres with narrow diameter distribution are obtained. Kinetic measurements revealed that in the dispersion pseudoanionic (initiator $(CH_3CH_2)_2AlOCH_2CH_3$) and anionic (initiator $(CH_3)_3SiONa$) polymerizations of ε-caprolactone the overall rates of monomer conversion are from 10 to 30 times higher than for the corresponding polymerizations in solution (THF solvent). Analysis of kinetic equations indicated that the observed faster monomer conversions in polymerizations in dispersed systems are due to the high local concentrations of active centers and monomer in growing microspheres.

INTRODUCTION

There are numerous papers on radical polymerization in dispersed systems. On the other hand, very little is known on similar processes with propagation on ionic and/or pseudoionic active species. Some of the differences between radical and ionic (or pseudoionic)

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polymerizations in dispersion are obvious. In radical processes active centers are generated continuously, either in solution or inside of particles (often swollen with monomer). In ionic and/or pseudoionic dispersion polymerizations, especially in the living ones, the active centers created at the very beginning are present during particle nucleation, growth and, if it happens, during particle aggregation. In radical polymerization, at any moment, there are no more than few macroradicals simultaneously present in the particle. On the contrary, in ionic dispersion polymerizations every growing particle contains thousands of propagating macromolecules. The confinement of active centers in small volume may result in formation of various aggregates of active centers affecting kinetics of polymerization.

Number of papers on ionic and pseudoionic polymerizations is very limited. The first one was published by Penczek et al. already in 1968 (Ref. 1). Shortly later synthesis of microspheres by ring-opening polymerization of cyclic monomers was patented (Ref. 2). Few years ago we began systematic studies of ring-opening polymerization of lactides (LA) and ε-caprolactone (CL) (Refs 3-6). Copolymerization in dispersed systems was reported for CL and glycolide (Ref. 7). Recently El-Aasser et al. presented results of the studies on anionic living polymerization of styrene (Ref. 8). In spite of certain progress in development of synthetic procedures for anionic and pseudoanionic polymerizations yielding microspheres with a narrow distribution of particle diameters little is known on the mechanism and kinetics of particle formation. In this paper we present results of our studies on these subjects.

RESULTS AND DISCUSSION

Particle Formation in Polymerization of ε-Caprolactone and Lactides

Polymerizations of CL and L-LA (L- isomer) were carried out in the presence of poly(dodecyl acrylate)-g-poly(ε-caprolactone) in 1,4-dioxane:heptane mixtures in a way described in our earlier papers (Refs 3-6). Tin(II) 2-ethylhexanoate was used for initiation of the polymerization of L-LA. Polymerizations of CL were initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ and $(CH_3)_3SiONa$. Samples of reaction mixtures were collected at the predetermined time moments for further analysis. In the case of polymerization of CL initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ we monitored partition of aluminum atom containing active centers between liquid and solid phases (microspheres) and, parallel, variation of $\overline{M}_n$ of poly(CL) in particles. Results of these determinations are shown in Figure 1.

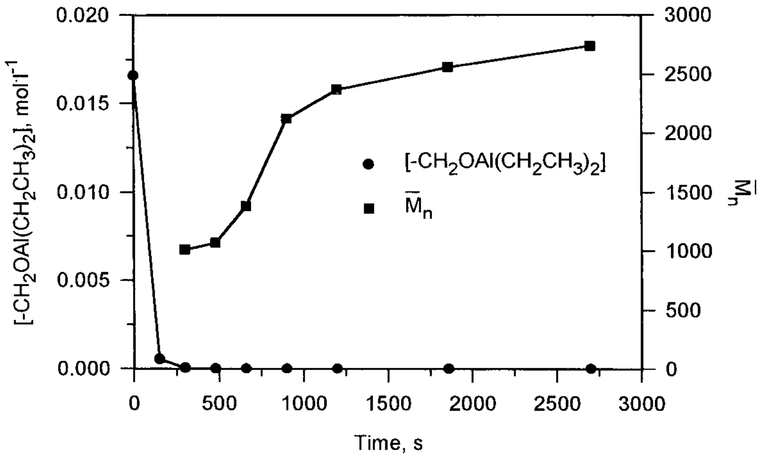

Figure 1 Dispersion polymerization of CL. Changes in concentration of $-CH_2OAl(CH_2CH_3)_2$ in solution and of $\overline{M}_n$ of poly(CL). Conditions of polymerization: $[CL]_o = 0.41$ mol/l, $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 1.66 \cdot 10^{-2}$ mol/l. (Reproduced with permission from Ref. 5)

From plots in Figure 1 it is evident that after about 300 s, when molecular masses of poly(CL) reach ca 1000, active centers disappear from solution. At the same moment we noticed the onset of turbidity of reaction mixture and by microscopic observations we found that poly(CL) microspheres were formed. After this initial period a further increase of $\overline{M}_n$ is due to propagation inside of particles. The discussion about the two stages of polymerization are illustrated in Figure 2.

One important parameter characterizing dispersion polymerizations is the number of particles in an unit volume of reaction mixture. Fast nucleation of microspheres, completed during initial period of monomer conversion, and constant number of particles during later stages of polymerization characterize processes yielding particles with narrow diameter polydispersity (Ref. 9). Number of particles in reaction mixture of polymerizing L-LA was determined by using a Bürker cell. Bürker cell (usually used for counting various blood cells) allows microscopic observations of particles present inside of rectangular parallelepiped with known volume ($2.5\cdot10^{-4}$ μl). Pictures were registered with a camera mounted on a microscope and then they were computer analyzed using a Multiscan 6.08 software provided by Computer Scanning Systems (Poland).

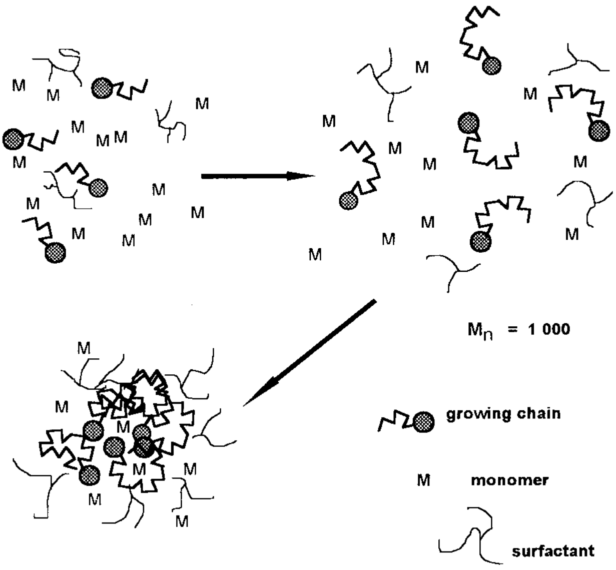

Figure 2 Scheme illustrating formation of microspheres during polymerizations of LA and CL in 1,4-dioxane:heptane mixtures. Particles nucleated by precipitation of growing macromolecules are stabilized with poly(dodecyl acrylate)-g-poly(ε-caprolactone)

Relation between the number of microspheres in 1 μl of reaction mixture and time of the polymerization of L-LA initiated with tin(II) 2-ethylhexanoate is illustrated in Figure 3. Plot in Figure 3 indicates that the number of particles, after initial increase, is constant during later stages of the polymerization (i.e., the delayed nucleation and aggregation are absent). As it was expected, the polydispersity of diameters of microspheres obtained in dispersion polymerization of L-LA proceeding with fast nucleation and absence of aggregation was narrow ($\overline{D}_v / \overline{D}_n < 1.1$, where $\overline{D}_n$ and $\overline{D}_v$ denote the number and volume average diameters of microspheres).

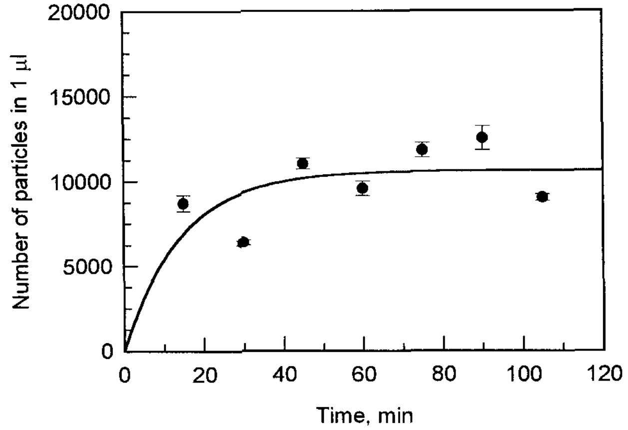

Figure 3 Number of particles in 1 μl of polymerizing mixture in dispersion polymerization of L-LA. Conditions of polymerization: L-LA 6.0 g, tin(II) 2-ethyl hexanoate 0.29 g, poly(dodecyl acrylate)-g-poly(ε-caprolactone) 0.24 g, 1,4-dioxane 30 ml, heptane 120 ml, temperature 90 °C

Kinetics of the Pseudoanionic and Anionic Dispersion Polymerizations of ε-Caprolactone

Kinetics of the dispersion polymerization of CL was investigated for processes initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ and $(CH_3)_3SiONa$. Polymerizations were carried out at room temperature in 1,4-dioxane:heptane (1:9 v/v) medium. Samples of reaction mixture, containing in addition dodecane (0.6 v%) used as an internal standard for GPC analysis, were collected at required time moments. Immediately afterwards they were added to THF containing acetic acid ($4 \cdot 10^{-4}$ mol/l) which killed active centers and stopped propagation. Monomer content in this solution was determined by GLC method. We found that kinetic polymerization can be formally described by similar equation as for the polymerization in solution:

$$\ln\{[CL]_o/[CL]\} = k_{p,d}^{app}[I]_o\, t \qquad (1)$$

where $[CL]_0$ and $[CL]$ denote the initial and actual monomer concentrations, $[I]_0$ denotes the initial concentration of initiator, t time, and $k_{p,d}^{app}$ denotes parameter called the apparent propagation rate constant in dispersed system. In equation (1) we omitted the equilibrium monomer concentration because on the basis of enthalpy and entropy of the polymerization of CL (polymerization in THF, ΔH_p = -28.8 kJ/mol, ΔS_p = -53.9 J/mol·K (Ref. 10)) we estimated that $[CL]_e < 5.9 \cdot 10^{-3}$ mol/l and thus, for initial monomer concentration $[CL]_0$ = 0.4 mol/l such simplification was justified for monomer conversion up to 90%.

We would like to stress that $k_{p,d}^{app}$ is a complex parameter depending not only on equilibrium between various kinds of active centers but also on transport of monomer molecules into the microspheres. At the moment we cannot present any data related to the mentioned equilibria between various physical forms (possible aggregated and nonaggregated species), however, determination of $k_{p,d}^{app}$ allows to compare the global rates of polymerizations in solution and in dispersions for the same initial concentrations of monomer and initiator averaged over the whole volume of reaction mixture.

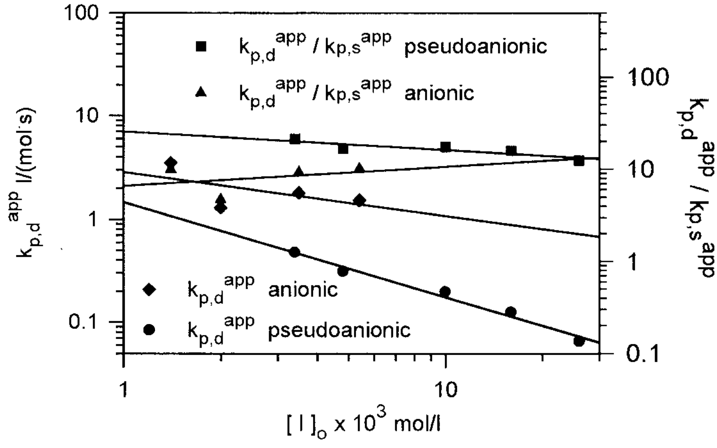

Figure 4 Dependencies of the apparent propagation rate constants ($k_{p,d}^{app}$) and ratios $k_{p,d}^{app} / k_{p,s}^{app}$ on concentration of initiator. Conditions: $[CL]_0$ = 0.4 mol/l, temp. 25 °C. Data for polymerizations in solution from Ref. 11 and 12)

Dependencies of $k_{p,d}^{app}$ and $k_{p,d}^{app} / k_{p,s}^{app}$ (where $k_{p,s}^{app}$ denotes the apparent propagation rate constant in solution (THF)) on concentration of initiator, for polymerizations initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ and $(CH_3)_3SiONa$, are illustrated in Figure 4. Plots in Figure 4 indicate that for similar concentrations of initiators (averaged over the whole volume of reaction mixture) the polymerizations in dispersed systems are characterized by the apparent propagation rate constants which are from 10 to ca. 30 times higher than for the corresponding polymerizations in solution.

We were interested in explanation whether the higher rates of polymerizations in dispersions should be related to the higher reactivity of active species or to another factors characterizing polymerizations in nonhomogeneous systems. For this purpose we analyzed kinetic equations for polymerizations in dispersions with fast initiation, fast nucleation of microspheres and absence of termination reactions.

For a system in which we have microspheres suspended in liquid medium the total volume of reaction mixture (V) and the total number of moles of monomer present at any given moment (m) can be expresses as:

$$V = V_m + V_s \qquad (2)$$

$$m = m_m + m_s \qquad (3)$$

where indices *m* and *s* relate these quantities to microspheres and to the liquid phase. Thus, the concentration of monomer averaged over the whole volume of polymerizing mixture can be written as:

$$[M] = \frac{m}{V} = \frac{V_m}{V}[M]_m + \frac{V_s}{V}[M]_s \qquad (4)$$

where $[M]_m$ and $[M]_s$ denote monomer concentrations in microspheres and in solution.

For concentration of active centers (in this analysis we do not discriminate between various possible physical forms of these species) averaged over the whole volume of reaction mixture ($[I]_o$) we can write:

$$[I]_o = \frac{i}{V} = \frac{V_m}{V}[I]_m \tag{5}$$

In equation (5), *i*, and $[I]_m$ denote number of moles of propagating species (assumed to be equal to the number of moles of an initiator; assumption of quantitative initiation with formation of one propagating center by one molecule of initiator) and local concentration of active species in microspheres, respectively.

Taking into account equation (4) we can write a set of differential equations describing variations of [M] with time:

$$\frac{d[M]}{dt} = \frac{1}{V}\frac{d(V_m[M]_m)}{dt} + \frac{1}{V}\frac{d(V_s[M]_s)}{dt} \tag{6}$$

$$\frac{d(V_s[M]_s)}{dt} = -S_m F_{s,m}[M]_s + S_m F_{m,s}[M]_m \tag{7}$$

$$\frac{d(V_m[M]_m)}{dt} = -V_m k_{p,m}{}^{app}[I]_m[M]_m + S_m F_{s,m}[M]_s - S_m F_{m,s}[M]_m \tag{8}$$

In these equations $k_{p,m}{}^{app}$ denotes the apparent propagation rate constant in microspheres, S_m total surface of microspheres, $F_{s,m}$ and $F_{m,s}$ coefficients characterizing flux of monomer molecules from solution into microspheres and from microspheres into solution, respectively.

By substituting for $d(V_s[M]_s)/dt$ and $d(V_m[M]_m)/dt$ in equation (6) expressions from equations (7) and (8), and taking into account relation given in equation (5) we obtained:

$$\frac{d[M]}{dt} = -k_{p,m}{}^{app}[I]_o[M]_m \tag{9}$$

Thus, the rate of monomer conversion averaged over the whole volume of reaction mixture depends on the averaged concentration of active centers ($[I]_o$) and on the local concentration of monomer in microspheres ($[M]_m$).

At the stationary state ($d(V_m[M]_m)/dt = 0$)

$$[M]_m = \frac{S_m F_{s,m}}{k_{p,m}^{app} V[I]_o + S_m F_{m,s}} [M]_s \qquad (10)$$

Combining equations (2) and (4) with equation (10) gives:

$$[M]_m = \frac{S_m F_{s,m}}{S_m [F_{m,s} + \alpha (F_{s,m} - F_{m,s})] + (1-\alpha) k_{p,m}^{app} [I]_o} [M] \qquad (11)$$

where $\alpha = V_m/V$ denotes volume fraction occupied by microspheres.

By substituting for $[M]_m$ in equation (9) the relation given in equation (11) we obtained:

$$\frac{d[M]}{dt} = - \frac{S_m F_{s,m} k_{p,m}^{app}}{S_m [F_{m,s} + \alpha (F_{s,m} - F_{m,s})] + (1-\alpha) k_{p,m}^{app} [I]_o} [I]_o [M] \qquad (12)$$

Thus, for $k_{p,d}^{app}$ in equation (1) we can write eventually:

$$k_{p,d}^{app} = \frac{S_m F_{s,m} k_{p,m}^{app}}{S_m [F_{m,s} + \alpha (F_{s,m} - F_{m,s})] + (1-\alpha) k_{p,m}^{app} [I]_o} \qquad (13)$$

When propagation in microspheres is much faster than diffusion of monomer molecules through the surface of microspheres (into and outside) the rate of polymerization becomes diffusion controlled and thus, independent from the initial monomer concentration:

$$\frac{d[M]}{dt} = - \frac{S_m F_{s,m}}{(1-\alpha)} [M] \qquad (14)$$

In the case of slow propagation in microspheres ($(1-\alpha)k_{p,m}^{app} << S_m[F_{m,s} + \alpha(F_{s,m} - F_{m,s})]$)

$$k_{p,d}^{app} = \frac{\frac{F_{s,m}}{F_{m,s}}}{(1-\alpha)+\alpha\frac{F_{s,m}}{F_{m,s}}} k_{p,m}^{app} \qquad (15)$$

For systems with $F_{s,m} = F_{m,s}$, i.e. when coefficients characterizing flux of monomer molecules into and outside of microspheres are equal $k_{p,d}^{app} = k_{p,m}^{app}$. For these systems the rates of polymerizations in solution and in dispersion should be the same for the same concentrations of initiator.

When microspheres occupy small fraction of the whole volume of reaction mixture ($\alpha << 1$) and when flux of monomer molecules into microspheres faster than the flux from microspheres into solution (to the extent that the relation $\alpha\frac{F_{s,m}}{F_{m,s}} >> 1$ is fulfilled) then the formula (15) is reduced to:

$$k_{p,d}^{app} = \frac{1}{\alpha} k_{p,m}^{app} \qquad (16)$$

In the case of the investigated polymerizations of CL we can conclude that propagation in dispersions is not controlled by slow diffusion of monomer molecules into microspheres. First of all, the apparent propagation rate constants for polymerizations in dispersed systems were found to be higher than for the corresponding polymerizations in solution (cf. Figure 4). Moreover, for polymerizations controlled by diffusion one should expect acceleration due to increased surface of microspheres during propagation (cf. equation (14)). Therefore, it is reasonable to assume that in dispersion polymerization of CL the limiting step is not the monomer diffusion into microspheres but its conversion into polymer inside of particles. Thus, the apparent propagation rate constant for dispersion polymerization of CL could be described by equation (14) or, for small volume fraction of microspheres, by equation (16).

In the case of polymerizations of CL investigated in our studies volume fraction of CL constituted ca. 5% at the beginning of the polymerization. For microspheres highly swollen with CL (1,4-dioxane:heptane 1:9 v/v mixture is a bad solvent for CL which at concentration 0.4 mol/l used in kinetic experiments was at the limit of its miscibility with this mixture) we can assume that the volume fraction of growing microspheres does not differ very much from the volume fraction of monomer $(\alpha \approx 0.05)$. Thus, the rate constants of propagation in microspheres $(k_{p,m}{}^{app})$ should be ca. 20 times smaller than $k_{p,d}{}^{app}$. Remembering on the relations between the apparent propagation rate constants for polymerizations in dispersion and in solution (cf. Figure 4, in which $10 \leq k_{p,d}{}^{app} / k_{p,s}{}^{app} \leq 30$) we can evaluate similar relations for the propagation rate constants for polymerization in microspheres, for which $0.5 \leq k_{p,m}{}^{app} / k_{p,s}{}^{app} \leq 1.5$. This means that values of the propagation rate constants in microspheres do not differ very much from the propagation rate constants for the polymerizations in solution. Thus, we can conclude that not the unusually high propagation rate constants for polymerizations in microspheres are responsible for high rates for polymerizations in dispersed systems but the high local concentration of active species and monomer in particles maintained during polymerization.

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