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Radical Polymerization Initiated from a Solid Substrate. 3. Grafting from the Surface of an Ultrafine Powder

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ABSTRACT: Kinetics of grafting radical polymerization of styrene and methyl methacrylate from the surface of titanium dioxide powder has been studied. Polymerization was initiated by hydroperoxide macroinitiator attached to the surface of the TiO_2 particles. The rate of grafting is linearly proportional to the rate of the initiation reaction from the surface. The fraction of the grafted polymer in the total polymer yield depends on the chain transfer reaction and on the mechanism of chain termination (combination or disproportionation). A mathematical model of the process has been used to explain the kinetics. The Trommsdorff effect has been found for the case of methyl methacrylate graft polymerization when the grafting amount approached high values. The regime of the multilayer coating formation has been studied in model experiments in the presence of macroinhibitor with the powder before coating by PMMA.

1. Introduction

Tethered polymer layers on the surface of ultrafine particles affect the colloidal stability of the particles in different surroundings and adhesion in various particle-filled polymer composites. Both problems are of great importance for numerous applications and have been the subject of fundamental research for a long time. Synthesis of a tethered polymer in situ on the particle surface is an alternative to the grafting of a previously prepared polymer to the solid surface. It is assumed that this method allows one to approach a higher density of a polymer brush, such as in the case of a “grafting to” process. Grafting from the surface has been shown to have interesting possibilities, especially for ultrafine particles, which usually form aggregates. It was assumed[1] that synthesis of the polymer coating in situ should be more preferable for obtaining a uniform coating of each particle because of the substantially higher accessibility of the interparticle space in aggregates for molecules of a monomer than for macromolecules.

In the companion papers,[2] we proposed the kinetic model of and gave experimental data for grafting by radical polymerization from a flat surface. It was also mentioned that for the polymerization located in a space restricted by two neighboring walls, the concentration profile of nonattached free radicals (free radicals in the bulk − monomer or solution) is homogeneous if the distance between the walls is less than 2 μm. The latter allows one to study kinetics of grafting in the very concentrated suspensions that are necessary to reach a high ratio between particle surface and monomer volume. The highly concentrated suspension cannot easy be agitated. Nevertheless, the above-mentioned kinetic regime allows one to study the grafting process in a sediment of the particles by applying a traditional method of measurement of monomer conversion, e.g., calorimetry, if the radius of a pore in the sediment is not larger as 1−2 μm. At a random packing of spherical particles, the radius of pores should be on the order of the particle radius value.

The goal of this paper was to study grafting polymerization on a surface of pores in a sediment formed by ultrafine particles and take the opportunity of this specific kinetic regime to investigate the mechanism of the process. In the paper, we report on the polymerization of styrene and methyl methacrylate (MMA) initiated from the surface of particles of the titanium dioxide pigment of a radius about 0.5 μm. Such particles fit the above-mentioned requirement for the size of pores in the sediment. The shape of pores cannot be easily modeled by a sphere or a cylinder. However, in the regime employed, the shape of pores is not important because there is no gradient of radical concentration profile between the walls. Consequently, even the model of infinite surfaces can be applied to particles of powder if the distance between the surfaces of particles less than 2 μm.

We used an initiation reaction which yields only attached free radicals. It was shown elsewhere[3] that the initiating system based on hydroperoxide + copper naphthenate ($CuNaphth_2$) provides free radicals according to the equations

$$ROOH + Cu^{2+} \rightarrow ROO^* + Cu^+ + H^+$$

$$ROOH + Cu^+ \rightarrow RO^* + Cu^{2+} + OH^-$$

Therefore, according to this scheme, when attached to the solid substrate, hydroperoxide yields only bonded

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free radicals. In this work, we used a hydroperoxide macroinitiator adsorbed on the surface of the titanium dioxide powder. As macroinitiators, we used the copolymer of hydroperoxide vinyl monomer, butylacrylate, and acrylic acid. It was shown that the adsorption of such macroinitiators on a solid surface of different oxides is a suitable way to immobilize the initiator of radical graft polymerization.[4] We take the opportunity to use the macroinitiator to attach hydroperoxy groups to the surface of titanium dioxide particles.

The grafting process may be summarized by the following kinetic scheme:

$$I_s \xrightarrow{k_d^s} R_s^* \quad \text{initiation on the surface}$$

$$R_s^* + nM \xrightarrow{k_p} R_s^* \quad \text{propagation on the surface}$$

$$R_v^* + nM \xrightarrow{k_p} R_v^* \quad \text{propagation in the bulk}$$

$$R_s^* + R_v^* \xrightarrow{k_t} P_s + P_v \quad \text{termination on the surface}$$

$$R_v^* + R_v^* \xrightarrow{k_t} P_v \quad \text{termination in the bulk}$$

$$R_s^* + X \xrightarrow{k_x} R_v^* \quad \text{transfer on the surface}$$

$$R_v^* + X \xrightarrow{k_x} R_v^* \quad \text{transfer in the bulk}$$

where I_s is the surface attached initiator, R_s^* and R_v^* are the attached and nonattached free radicals, respectively, M is the monomer, X is the transfer agent, k_p, k_t, and k_x are the constants of propagation, termination, and transfer reactions, respectively, k_d^s is the constant of decomposition rate of the surface-attached initiator, and P_s and P_v are the grafted and ungrafted polymers, respectively.

In the kinetic scheme, ungrafted free radicals R_v^* appear because of the transfer reaction. We do not analyze the nature of a transfer agent X. It may be a monomer, solvent, or other ingredient of the reaction mixture. Ungrafted polymer appears from termination of (a) bulk free radicals or (b) a bulk free radical with an attached free radical due to termination reaction by disproportionation.

In the kinetic scheme, we assume that propagation, termination, and transfer reactions constants on the surface and in the bulk are the same.[2] In the companion papers, we have suggested the mathematical model describing the grafting process (see in the paper 1 Scheme 1). From the model, one can calculate the grafting rate, the rate of polymerization in the bulk, and the grafting efficiency (the ratio between amount of grafted polymer and total amount of the polymer produced in the process):

$$W_s = k_p[R_s^*][M] \tag{1}$$

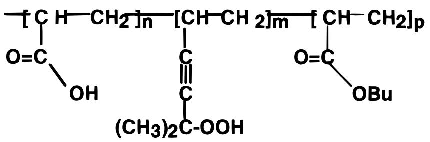
$$W_v = k_p[R_v^*][M] \tag{2}$$

$$E = W_s\psi/(W_v + W_s\psi) = \alpha\psi[R_s^*]/([R_v^*] + [R_s]\psi) \tag{3}$$

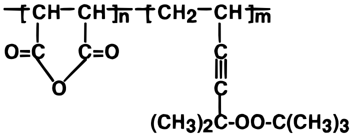
where W_s is the grafting rate (mol m^{-2} s^{-1}); W_v is the bulk polymerization rate (mol m^{-3} s^{-1}); E is the grafting efficiency; ψ = [specific surface (m^2/g)] × [fraction of TiO$_2$ powder (g/m^3)]. Parameter α depends on the termination mechanism: $\alpha = 1$ for combination and $\alpha = 0.5$ for disproportionation.

3. Experimental Section

Materials. The hydroperoxide macroinitiator[5] (HMI), a copolymer of hydroperoxide monomer 5-hydroperoxy-5-methyl-1-hexen-3-yne, butylacrylate, and acrylic acid ($m/n/p$ = 2:4:4 mole), M_n = 11 000, was obtained from the Department of Organic Chemistry of the Lviv Polytechnic State University and used without further purification:



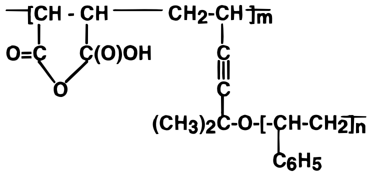
Polyperoxide macroinitiator[5,6] (PMI) copolymer of maleic anhydride and 5-*tert*-butyl-peroxy-5-methyl-1-hexen-3-yne (mol ratio 1:1)



M_n = 5000 was obtained from the Organic Chemistry Department of Lviv Polytechnic State University. 4,4′-Azoisobutyronitrile (AIBN) reactive grade was used as received.

The monomers styrene and MMA of reactive grade were distilled under reduced pressure in argon atmosphere. Butyl acetate (BA) and copper naphthenate CuNaphth$_2$ of reactive grade were used as received. Titanium dioxide TiO$_2$ (rutile modification, industry pigment, specific surface S = 1.5 m^2/g) was rinsed in BA and dried at 600 °C.

The macroinhibitor (MIn) was synthesized in two steps: (1) Bulk polymerization of St (40 wt % in the toluene solution) was initiated by PMI (2%) at 403 K for 5 h. In this step, we synthesized grafted polymer of the molecular mass 2 × 10^5. The structure of the polymer was not controlled. Our goal was to obtain the polymer of a high molecular weight functionalized by the anhydride groups:



(2) Functionalization of the grafted polymer was carried out by the reaction (room temperature, 100 h, solvent BA) of the anhydride groups with 2,2′,6,6′-tetramethyl-4-aminopiperidine-1-oxyl (Merck). The product was purified by precipitation in hexane. It was found from ESR spectra that 1 mol of stable free radicals weighs 160 000 g.

Attachment of the Hydroperoxide Macroinitiator. HMI was attached to the TiO$_2$ powder surface by adsorption from 0.9% solution in BA for the ratio of adsorbent/solution = 1:3 by weight, which corresponds to the adsorption amount of 0.3% (measured by pyrolysis at 773 K). The powder was separated by centrifugation, rinsed with BA to remove unadsorbed HMI, and dried at 353 K under reduced pressure.

Polymerization of St and MMA from the TiO$_2$ powder was performed in sealed glass ampules. The ampule was filled with the powder (2 g) and the monomer solution in BA (1 mol/L) under argon. Then, the ampule was placed into the cell of a differential isothermal calorimeter to measure heat of the polymerization at 313 K. Once the experiment was finished, the contents of reactive vessel were removed and rinsed six times in BA to wash out ungrafted polymer. The amount of the grafted polymer was evaluated by pyrolysis at 773 K.

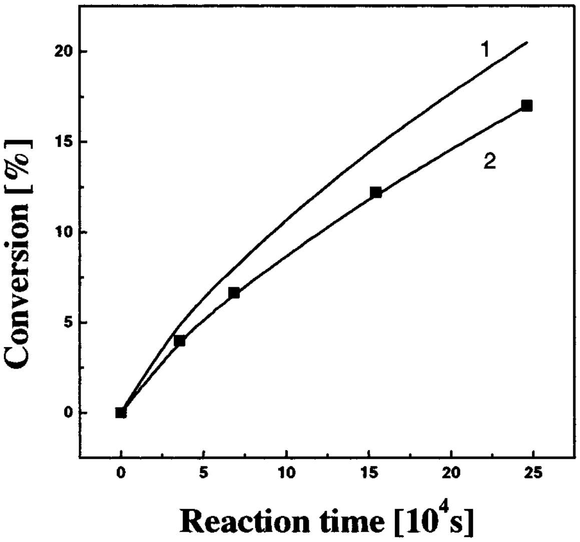


Figure 1. Grafting of styrene: (1) total conversion of styrene in the ampule and (2) conversion of styrene in grafting on the surface of TiO_2.

Decomposition of HMI in solution (0.5−5%) was studied in sealed ampules in the calorimeter cell at 413 K.

Processing of the Results of Calorimetry Measurements. The rate of the polymerization W (mol L^{-1} s^{-1}) was calculated using the Thian equation,[7]

$$W/[M] = (B/mq)(h + \tau\, dh/dt)$$

where $B = 5.04 \times 10^{-7}$ W/cm and $\tau = 98$ s are the calorimeter constants, [M] is the monomer concentration (mol/L); m is the monomer weight in a vessel (g); h is the amplitude of a signal at time t (s); q is the specific heat of the polymerization (716 J/g for styrene and 556 J/g for MMA[8]).

The rate of HMI decomposition was calculated in the same way; the specific decomposition heat of HMI was determined from the integral calorimeter curves.

4. Results and Discussion

Grafting of Styrene. Typical kinetic curves of styrene grafting polymerization are presented in Figure 1. The total PS conversion differs only slightly from the grafted amount of the polymer (compare curves 1 and 2). The grafting efficiency E amounts to 0.83. This fact is evidence of the existence of some amount of unattached free radicals in the bulk. It is interesting to compare these data with results reported earlier for styrene graft polymerization for which an initiator produced two sorts of free radicals: attached and unattached to the substrate.[9] In the latter experiments, E was found to be about 0.10.

By changing the catalyst concentration, we found the experimental dependence of the polymerization rate versus the initiator catalytic decomposition rate W_d. The experimental data are plotted in Figure 2 (squares). In the same figure (line), we plotted the dependence calculated from the kinetic model. We obtained similar values of the polymerization rate order on the rate of initiator decomposition from the experiments and the computations: 0.93 and 0.89, respectively. The calculations were provided for the following parameters: TiO_2 concentration = 2×10^6 g/m^3, $D = 1 \times 10^{-10}$ m^2/s, $I_S = 0.5 \times 10^{-5}$ mol/m^2, and $k_dS = 1 \times 10^{-5}$ s^{-1}; K_x[X] was used as a fit parameter and varied in the range 0.05−0.5 s^{-1}.

The constant of the chain transfer reaction to BA is 10 times larger than that for the reaction leading to styrene.[7] We change the monomer concentration in grafting experiments to change the rate of transfer reaction. The experimental and computed due to the model data are presented in Figures 3 and 4. The experimental values of E and W/[M] are plotted versus solvent concentration. Computed from the model, values are presented versus parameter K_x[X]. It is clear from the data that the grafting efficiency and the rate of grafting decrease as the rate of transfer reaction increases.

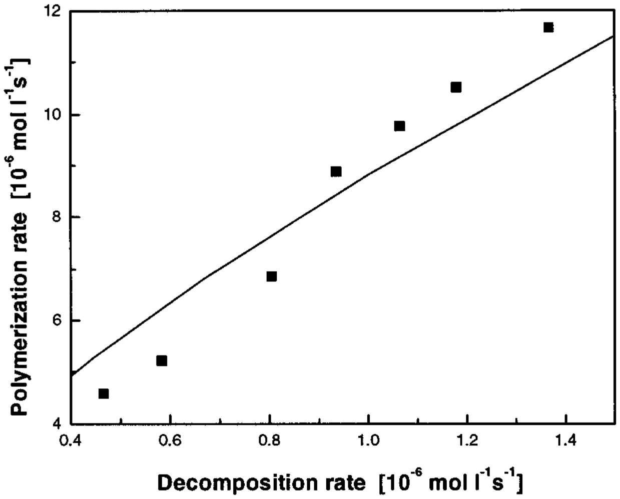


Figure 2. Dependence of polymerization rate W vs the HMI decomposition rate: line = calculations; full squares = experiment.

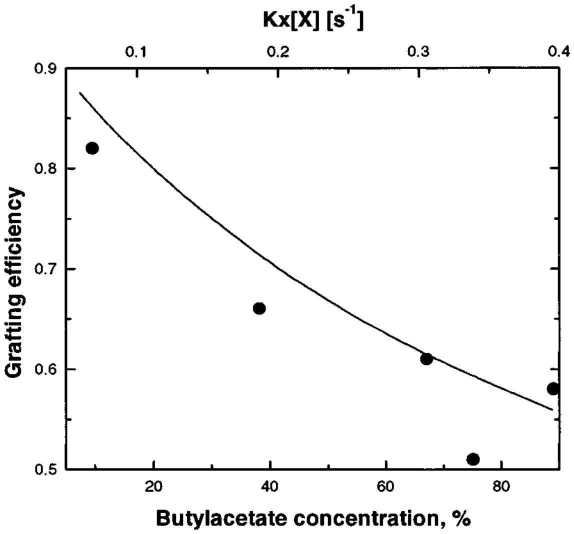


Figure 3. Dependence of the styrene grafting efficiency E vs (solid line) transfer parameter K_x[X] obtained from the model computations and vs (full circles) solvent concentration obtained in the experiment.

Consequently, the experimental data presented in Figures 2−4 are in good agreement with the model predictions and confirm the assumptions that (1) the initiation by adsorbed HMI + catalyst yields mainly attached free radicals and (2) attached free radicals terminated by transfer reaction yield the ungrafted polymer.

Grafting of Methyl Methacrylate. The kinetics data of MMA grafting are presented in Figure 5. Two differences from the styrene polymerization were found: (1) grafting efficiency was $E = 0.42$, which is 2 times less than that for PS grafting and is in good

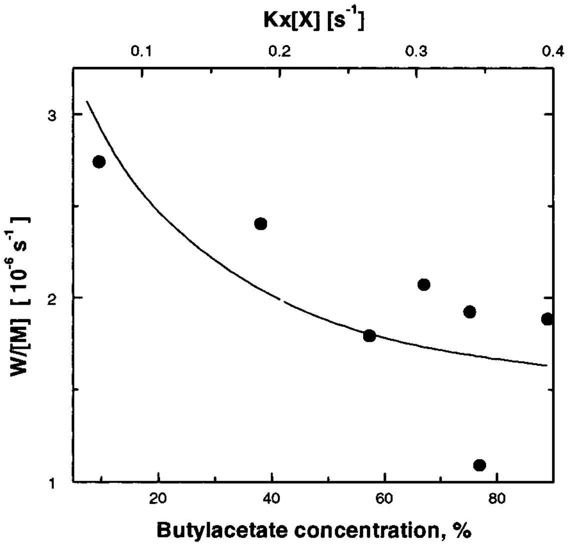


Figure 4. Dependence of the normalized rate of styrene polymerization $W/[M]$ vs (solid line) transfer parameter $K_x[X]$ obtained from the model computations and vs (full circles) solvent concentration obtained in the experiment.

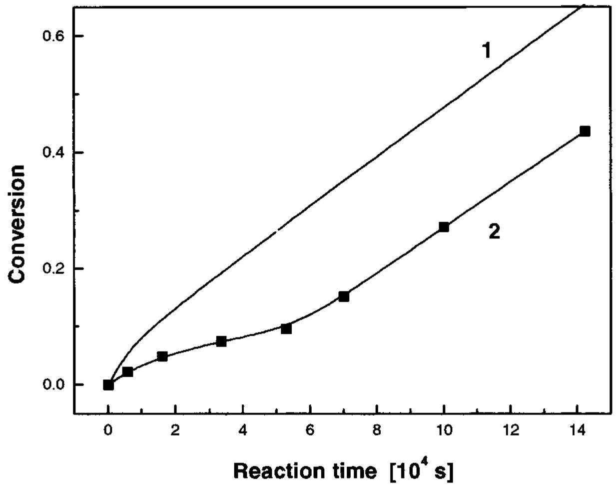


Figure 5. Grafting of MMA: (1) total conversion of styrene in the ampule and (2) conversion of styrene in grafting on the surface of TiO_2.

agreement with the theoretical calculation for the parameter $\alpha = 0.5$. Consequently, the disproportionation causes a decrease of grafting efficiency and an increase of the amount of the ungrafted PMMA. (2) After 4.5 h of the polymerization (8.1 mg/m^2 of PMMA grafting amount), the acceleration of the grafting (in the same manner as Trommsdorff effect) is observed. To study this phenomena, we performed the following experiments.

Multilayer Coating. Concentration of a grafted polymer in the stretched brush with a grafted amount on the order of 10 mg/m^2 corresponds to the volume fraction of the polymer in the layer of about 5% (as it was estimated in the companion paper). Such concentration of the polymer is critical with respect to conditions of the Trommsdorff effect in radical polymerization. We performed experiments to examine the possibility of formation of the grafted layers in conditions of the Trommsdorff effect.

Grafting of MMA was performed at 333 K in the presence of the macroinhibitor MIn (32 mg/mL), the initiator in the bulk AIBN (3×10^{-3} mol/L) and TiO_2 powder covered by different amount of polymer previously grafted on the surface. It was shown elsewhere[10] that the MIn effectively inhibits radical polymerization in the bulk but does not in the polymer layer. Consequently, one may perform polymerization inside the layer and inhibit the process outside (in the bulk).

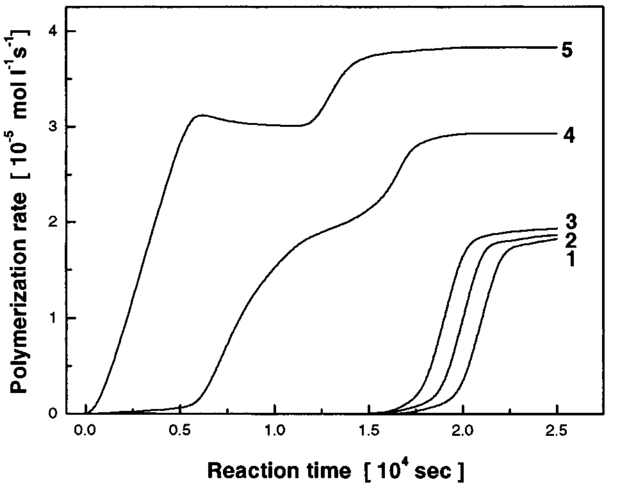


Figure 6. Kinetics of the MMA polymerization with MIn and (1) powder of TiO_2 uncovered, (2) adsorptionally covered by HMI, and covered with grafted PMMA: (3) 5, (4) 9, and (5) 25 mg/m^2.

Three samples of TiO_2 with different amount of the grafted PMMA (5, 9, and 25 mg/m^2) were prepared as described below, rinsed in solvent, and then used for the following experiments. The effects of ungrafted PMMA and free radicals in the bulk were eliminated in these experiments using MIn. As a reference, we also used uncovered TiO_2 powder and the powder covered by an adsorbed layer of HMI. The kinetics curves of MMA polymerization are shown in Figure 6.

The kinetic curves of the polymerization in the presence of the uncovered powder, covered by adsorbed HMI and the powder covered with 5 mg/m^2 of PMMA show very pronounced 5 h induction periods (see curves 1−3) caused by MIn. Consequently, in these cases, MIn completely inhibits the polymerization.

Opposing results were obtained for the highly loaded (25 mg/m^2 of PMMA) powder (curve 5). After a short time, the polymerization rate increased and reached a high value. The second step on the curve corresponds to the end of the induction period for the bulk polymerization. In the case of the powder coated with 9 mg/m^2 of PMMA, the polymerization kinetics exhibits some transitional behavior. (If a smaller-size inhibitor is used for the experiments, we obtain a very pronounced induction period for the every sample).

Consequently, we may suggest the following mechanism of the polymerization. The grafted polymer layer on the surface of the powder is swollen by the monomer solution. The initiator and MMA penetrate into the layer. The initiator starts the polymerization in the swollen polymer layer. If the layer is thin, the MIn inhibits the polymerization in the layer. If the layer is thick (more than 5 nm), the polymerization runs inside the layer. Because of the relatively high polymer concentration in the layer, the polymerization runs with an acceleration in the conditions of the Trommsdorff effect. The layer grows as a propagating front because of a slow, outward diffusion of chains from the layer.

5. Conclusions

Grafting of styrene and MMA from the surface of the titanium dioxide powder by radical polymerization mechanism was studied. The polymerization was initiated by the redox reaction of hydroperoxide macroinitiator physisorbed on the surface and copper naphthenate. This initiator yields only surface-attached free radicals. However, a substantial amount of polymer in the bulk was found. This result is evidence of the termination of grafted chains by transfer reaction.

The mathematical model based on the above-mentioned termination mechanism predicts dependence of the grafting efficiency and rate on the transfer parameter k_x[X]. The experimental data are in good agreement with the results of computations of this model.

The Trommsdorff effect mode was detected for the graft polymerization of MMA for a high amount of the grafted polymer on the surface. The model experiments performed in the presence of macroinhibitor and the powder previously covered with PMMA have shown that the polymer layer grows because of the polymerization of ungrafted chains inside the layer. This mechanism affects formation of a multilayer coating on the surface.

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