Silica-Filled Poly(HEMA) from Hema/Grafted SiO$_2$ Nanoparticles: Polymerization Kinetics and Rheological Changes

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ABSTRACT: The chemio-rheological behavior during the radical polymerization of the HEMA/grafted silica nanoparticles was found to be very dependent on the weight fraction of the silica particles. In the case of the neat HEMA reactive system, the macrogelation occurs at the same time as the Trommosdorf effect. The reactive groups on the silica nanoparticles, which have a lower reactivity compared to that of the HEMA monomer, slow down the mean radical polymerization rate of the filled reactive system. The reactions between the grafted groups of the neighboring silica particles lead to the percolation, i.e., macrogelation, of the reactive system at low conversion degree, even if the reactive system is kinetically at the stationary state. The reactive medium of the HEMA/grafted silica nanoparticles systems could be divided to two parts: the percolating nanoparticles part for which the polymerization rate is very slow, and the bulk HEMA medium in which the radical polymerization rate is the same order of magnitude than for the neat HEMA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2701–2713, 1999

Key words: grafted silica nanoparticles; radical polymerization; kinetic; rheological changes; gelation; vitrification; gel effect

INTRODUCTION

The concept used to combine both inorganic and organic chemistries leads to a wide field of applications in materials science. Numerous types of hybrid organic inorganic materials can be prepared from a sol-gel process in which both inorganic and organic parts contribute to the overall properties of the composite by their own properties. As a consequence, such hybrid materials may offer various potential applications in different fields such as nonlinear optics,[1] adhesives,[2] selective membranes,[3] coatings,[4] and composite materials. Three ways of synthesizing were reported in the literature to obtain such materials. The main process involves the hydrolysis and condensation reactions of metal alkoxide in the presence of a nonreactive polymer such as PVA or PMMA.[5–7] The second process consists in the hydrolysis and condensation of metal alkoxide in the presence of an organic monomer that could be polymerized.[8] The third way of synthesis consists of hydrolysis and condensation of alkoxy-functionalized oligomers.[9–12] Different parameters

Table I   Composition of the Various Reactive Systems Considered in this Study

	Weight Percent of SiO$_2$	Mol Number of SiO$_2$ Particles (10^{-5})	Molar Number of HEMA Monomer (mol)	Second Order Functionality f_w(*)	Mol Number of Double Bonds on the Particles Surface (10^{-2})	Molar Percent of Double Bonds on the Particles Surface
1	5	3.28	0.73	5.78	0.43	0.58
2	7.5	4.92	0.71	7.81	0.64	0.89
3	10	6.57	0.69	9.96	0.85	1.22
4	15	9.85	0.65	14.58	1.28	1.92
5	20	13.13	0.62	19.77	1.71	2.70
6	30	19.69	0.54	32.11	2.56	4.53

such as the amount and type of catalyst, the amount of water, and the molecular weight of the organic chains influence the kinetics of the sol-gel reactions, i.e., the hydrolysis and the condensation reactions.[13–15] As a consequence, the morphology and the properties of the resulting hybrid organic–inorganic materials are strongly dependent on the competition between the kinetics of the hydrolysis and condensation reactions leading to the formation of the inorganic rich phase and the thermodynamic of the phase separation between the organic-rich and the inorganic-rich components. The control of the phase separation in the nanoscale range offers the possibility to synthesize transparent composite materials or coatings with improved mechanical properties in comparison with the neat polymer (*in situ* filling). To avoid macroscopic phase separation and low mechanical properties, strong interactions between the organic and inorganic parts are required.[2,7,8] The use of appropriate coupling agent such as silicon alkoxydes, especially organosilanes, can lead to a continuum of chemical links at the interface between the inorganic-rich nanodomains and the continuous organic phase.

In the past few years, much interest in hybrid organic–inorganic materials based on polymers and pre-formed nanoparticles have been developed. This kind of hybrid material has potential applications as rejection filters, optical switches, tenable filters, etc.[16–19] The control of the nanoparticle dispersion in the organic matrix seems to be a limiting factor for improving the properties of this kind of material.

The aim of this article is to study the synthesis of the hybrid organic–inorganic materials based on methacrylate-grafted SiO$_2$ nanoparticles and a polymethacrylate matrix synthesized by free radical polymerization of HEMA. The control of the properties of the resulting material requires the knowledge of the kinetics of the radical polymerization and structural changes occurring during the polymerization. For that purpose, both rheological and calorimetric measurements were performed.

EXPERIMENTAL

Materials

The HEMA-modified silica nanoparticles (13 nm) were supplied by Hoechst as a dispersion in HEMA (30% wt silica). Dispersions with silica content varying from 20 to 5% wt silica were prepared by adding a HEMA monomer. The average functionality of particles is about 1300.

The compositions of the various dispersions are given in Table I. The calculation of the mean functionality, f_w, assumes that each particle is considered as a multifunctional molecule and can be calculated as follows:

$$f_w = \frac{n_{SiO_2} \cdot f_{SiO_2}^2 + n_{HEMA} \cdot f_{HEMA}^2}{n_{SiO_2} \cdot f_{SiO_2} + n_{HEMA} \cdot f_{HEMA}}$$

where n_{SiO_2} and n_{HEMA} are the molar numbers of the SiO$_2$ nanoparticles and HEMA monomer, respectively. f_{SiO_2} and f_{HEMA} are the functionalities of the SiO$_2$ nanoparticles and HEMA monomer, respectively.

The molar percentage of double bonds on the nanoparticles surface were calculated from the mole number of SiO$_2$ particles and the nanopar-

ticles functionality weighted by the total number of nanoparticles as follows:

$$X = \frac{n_{SiO_2} \cdot f_{SiO_2}}{n_{SiO_2} \cdot f_{SiO_2} + n_{HEMA}}$$

2-Hydroxyethyl methacrylate, HEMA, monomer was supplied by Aldrich Chemical (97.5% purity). It was used without any further purification and contained about 2% of dimethacrylate , EGDMA, as determined by chromatography.

The benzoyl peroxide, denoted BPO, supplied by Aldrich Chemical, was used as a thermal initiator for the radical polymerization.

Experimental Techniques

DSC was used to investigate the radical polymerization kinetics for all the systems using a Perkin-Elmer differential scanning calorimeter (DSC-7). Indium was used for temperature and calorimetric calibration. The procedure employed was as follows: a 3–8-mg drop of reactant containing the initiator was introduced into a DSC aluminium pan. Pans with holes were used to allow the radical polymerization to process under the inert atmosphere of the DSC oven (N_2 atmosphere). The weight loss during the experiment was negligible over the range of temperature employed ($50 < T < 60°C$). For samples containing SiO_2 particles, a pan containing the equivalent weight of SiO_2 powder was used as a reference to take into account the heat flow responsible on the heat of the inorganic part of the sample during the reaction. The exothermic heat flow measured during the reaction was converted into conversion and reaction rates as function of time. The time required for the completion of the curing was determined on the thermogram when the heat flow curve reached the initial values. The total heat generated was determined in the same conditions when the reaction proceeded in the scanning mode from room temperature to 220°C at the heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ (12.8 kcal · mol^{-1}).

Structural changes during the radical polymerization such as gelation or vitrification were evidenced by means of rheological measurements using a Rheometrics Dynamic Analyzer (RDA 700) in a parallel-plate mode. The reactive mixture was put between the 40 mm-diameter plates with a gap between 1 and 1.2 mm. Experiments were conducted with an oscillatory shearing in a frequency sweep mode (between 1 and 100 rad

· s^{-1}). To keep the reaction conditions similar to those of DSC, these measurements were conducted under nitrogen atmosphere. The strain amplitude was kept constant to 2.5%.

RESULTS AND DISCUSSION

The polymerization reaction of HEMA monomers occurs from the chain polymerization mechanism that typically consist in three steps: namely, initiation, propagation, and termination.

Initiation

Benzoyl peroxide is used to initiate the radical polymerization of HEMA. Its fragments generate free radicals:

Once produced, the free radical reacts rapidly with a molecule of monomer

$$R^\bullet + M \xrightarrow{k_i} M_1^\bullet$$

where k_i is the constant rate of the initiation reaction.

Propagation

This consists of the growth of the polymer molecule by consumption of monomer molecules,

$$M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet$$

$$M_2^\bullet + M \xrightarrow{k_p} M_3^\bullet$$

$$M_3^\bullet + M \xrightarrow{k_p} M_4^\bullet$$

i.e.,

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

where k_p is the constant rate of the propagation reaction.

Termination

The growing polymer chains do not continue their growth until total consumption of the monomers molecules. It looses their initial reactivity by termination reactions that occurs by combination:

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{tc}} M_{n+m}$$

or by disproportion

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{td}} M_n + M_m$$

k_{tc} and k_{td} are rate constants of the of recombination and disproportionation reactions, respectively.

As previously mentioned, silica nanoparticles are functionalized by methacrylate groups, and thus, may copolymerize with the free HEMA monomers of the suspension medium.

The radical polymerization on the surface of SiO_2 particles between two neighboring groups can also occur,

HEMA Polymerization

Figure 1 displays the DSC thermogram leading to the isothermal reaction rate, v_p, and the conversion of the double bonds at different temperatures for the HEMA polymerization. In Figure 1(a), the gel effect is clearly observed after the stationary state when v_p remains constant. In the stationary state, the rate of decomposition of the initiator, v_d, and the rate of terminaison reaction, v_t, are equal. Thus, the radical concentration is constant in the stationary state. As the viscosity of the system increases, v_t decreases, and as a consequence, the balance between consumption and the appearance of radicals is changed, leading to an increase of the radical concentration and to a higher rate of polymerization. The polymerization rate is thermally activated, and the activation energy is found to be about 14 kcal · mol^{-1}. This value is in agreement with those reported in the literature.[20]

Figure 2 gives the dependence of the storage shear modulus, G', with the reaction time during the HEMA radical polymerization at 60°C. The large increase of the storage modulus observed from 10 min could be associated to the macrogel formation as demonstrated by looking to the appearance of the insoluble fractions in tetrahydrofurane and methyl-ethyl-ketone. The gelation is followed by the vitrification of the reactive system. The appearance of the macrogel could be associated with the presence of dimethacrylate as contaminant resulting from the HEMA synthesis, and to transfer reactions on PHEMA chains during the polymerization. This low amount of dimethacrylate enables one to lead to a crosslinked structure, as reported by Dusek.[21] In addition, some transfer reactions on the hydroxy ethyl groups can occur.

The increase of the storage modulus associated with the gelation phenomena is consistent with the DSC measurements (Fig. 2). This effect confirms the fact that the increase of the viscosity disturbs the balance between the appearance and the consumption of the radicals leading to the gelation effect.

Polymerization of HEMA in the Presence of Methacrylate-Grafted Silica Nanoparticles

The isothermal reaction rate, v_p, and the conversion of double bonds for reactive systems based on HEMA and HEMA-grafted SiO_2 with different amount of silica are reported in Figure 3.

(a)

(b)

Figure 1   (a) Reaction rate of the HEMA radical polymerization at different temperatures, determined by DSC: ($\triangle$): 50°C; ($\times$): 55°C; ($\bigcirc$): 60°C. (b) Conversion vs. reaction time for the HEMA polymerization at different temperatures, determined by DSC: ($\triangle$): 50°C; ($\times$): 55°C; ($\bigcirc$): 60°C.

Figure 2 Superimposition of the reaction kinetics and the rheological changes during the radical polymerization of HEMA at 60°C (frequency: 1 rad/s).

It can be seen that the radical polymerization is slowed down by the introduction of the SiO_2 particles even if the mean functionality of the mixture increases (Table I). In addition, the final conversion decreases as the percentage weight of SiO_2 particles increases.

The first trend is opposite to the results observed in the literature as multifunctional organic monomer was added to a difunctional one. In the later case, the gel effect is observed earlier. This phenomena can be explained by the fact that the methacrylate functions attached to the silica surface have a lower mobility and as a consequence, a lower reactivity than those from a multifunctional organic monomer. In fact, a multifunctional organic monomer having high mobility lead more rapidly to gelation.[22–24]

To confirm the hypothesis of a lowest reactivity of the methacrylate groups from the silica surface, the polymerization kinetics in the presence of nongrafted SiO_2 nanoparticules was studied. Figure 4 displays the comparison between the polymerization rates and the conversion changes during the reaction time for the methacrylate-grafted and nongrafted SiO_2-filled systems. It can clearly be seen that the polymerization rate is slowed down in the case of the grafted nanoparticule-filled system in comparison with the reactive system based on the nongrafted nanoparticules. This fact confirms that the grafted methacrylate group on the particle surface has a low reactivity because of its lower mobility. In addition, for the same weight fraction of filler, i.e., 10 wt %, the final conversion for the grafted nanoparticule-filled system is lower than that of the reactive system with nongrafted nanoparticules, confirming the previous interpretations. The lower polymerization rate and final conversion for the nongrafted nanoparticule-filled system in comparison with the neat HEMA could be attributed to the effect of the adsorbed water and other impurities at the hydrophilic surface of the silica, which could slow down the polymerization rate.

The changes of the storage modulus, G', with the reaction time for the filled systems are reported in Figure 5. The conversion at the gel point was deduced from the conversion vs. reaction time curves after determination of the gelation time (Fig. 6). It can be seen that adding multifunctional SiO_2 particles leads to a faster appearance of the macroscopic gelation. In fact, the increase of the elastic response occurs for a shorter

(a)

(b)

Figure 3 (a) Reaction rate of the HEMA/grafted SiO_2 reactive systems at 60°C. (b) Conversion vs. reaction time for the HEMA/grafted SiO_2 reactive systems at 60°C.

time than for the neat HEMA system (Table II). Owing to their high functionality, the addition of SiO_2 particles favors the percolation, and as a consequence, the gelation occurs at very low conversions in comparison with the neat HEMA system (Table II).

(a)

(b)

Figure 4 (a) Comparison of the radical polymerization rate between the reactive systems filled with grafted and nongrafted SiO_2 nanoparticles. ($\triangle$): neat HEMA, ($\diamond$): nongrafted nanoparticles, ($\times$) grafted nanoparticles. (b) Comparison of the conversion degree evolution during the radical polymerization between the reactive systems filled with grafted and nongrafted SiO_2 nanoparticles. ($\triangle$): neat HEMA, ($\diamond$): nongrafted nanoparticles, ($\times$) HEMA-grafted nanoparticles.

Figure 5 Comparaison of the reaction kinetics and the rheological changes during the radical polymerization of the HEMA/grafted SiO_2 systems with 15% wt of silica at 60°C (frequency: 1 rad/s).

It can be seen in Figures 5 and 6 that after gelation, the filled systems display an intermediate pseudoplateau on the storage shear modulus vs. time curve that is associated with that of a filled elastomeric network. In the rubbery state, the rubber modulus increases as the content of SiO_2 increases. The time width, i.e., the time for which the rubbery modulus remains roughly constant, also increases with increasing the SiO_2 content (Table III). In addition, the reactions occuring during this pseudoplateau contribute to a large increase of the storage modulus with time of reaction as the content of SiO_2 increases. After this rubbery plateau, i.e., for longer times of reaction, the storage modulus increases again, indicating that the vitrification occurs. By comparing the DSC and rheological data, one can see that during the time range corresponding to this "plateau" the polymerization rate remains constant, and the reactive system is in the stationary state. The autoacceleration observed by DSC leads to a large increase of the conversion responsible of the vitrification (Fig. 5).

In the case of the neat HEMA polymerization, i.e., without SiO_2 particles, the observed autoac-

celeration phenomenon leads to the gelation, then to the vitrification of the polymer. As a consequence, the polymerization kinetics and the rheological behavior of the reactive system are interdependent. In fact, the increase of conversion during polymerization leads to an increase of the viscosity, which modifies the ratio between the initiator decomposition and radical termination reaction rates. The radical concentration increases and the consumption of the monomer also increases, leading to an autoacceleration phenomenon.

When SiO_2 particles were added to the HEMA monomer, the macrogel was formed at shorter times and lower conversions. The gelation phenomena could be explained by the SiO_2 particle percolations owing to their high functionality in opposition to an autoacceleration phenomena as in the case of neat HEMA.

From these observations, the reactive sites of grafted silica systems can be divided in two types: those grafted on the SiO_2 surface, which have a low reactivity and can contribute to the percolation of the system for a low conversion, and those from the bulk HEMA medium for which the rad-

Figure 6 Dependence of the storage shear modulus, G', with the conversion for the radical polymerization of the filled systems at 60°C (frequency: 1 rad/s). (◆): neat HEMA, (+): 5% wt SiO$_2$, (◇): 7.5% wt SiO$_2$,: (△): 10% wt SiO$_2$, (×): 15% wt SiO$_2$ (□): 20% wt SiO$_2$,: (○): 30% wt SiO$_2$.

ical polymerization proceeds as for the neat HEMA. For this type, the autoacceleration phenomena could be observed.

These observations can be stressed by the analysis of the morphology using transmission electron microscopy, TEM (Fig. 7). In fact, these silica-filed materials exhibit a morphology based on spherical elementary particles having a diameter close to 13 nm associated as aggregates (presence of larger dark regions) of nearly 100 nm in size.

To express the copolymerization rate at the glassy state, Zhu et al.[25,26] suppose that two populations of radicals in the reacting medium may exist—the "shielded," and the reactive radicals. The propagation rate was expressed as:

$$v_p = (k_{p(\text{shielded})}[R^{\bullet}]_{\text{shielded}} + k_{p(\text{active})}[R^{\bullet}]_{\text{active}}) \cdot [M]$$

In the case of the reactive systems considered in this study, the polymerization rate on the silica surface is very low compared to that in the bulk HEMA. As a consequence, the polymerization rate, in the stationary state, of the filled reactive systems could be expressed as follows:

$$v_p = v_{p(\text{HEMA})} + v_{p(\text{SiO}_2)}$$

$$v_p = k_{p(\text{HEMA})} \cdot [M] \cdot [R^{\bullet}]_{(\text{HEMA})}$$
$$+ k_{p(\text{SiO}_2)} \cdot [M] \cdot [R^{\bullet}]_{(\text{SiO}_2)}$$

Table II   Conversion Fat the Macrogelation for the Reactive Systems Containing Different Amounts of Grafted SiO$_2$ Particles (at 60°C)

SiO$_2$ (% wt)	0	5	7.5	10	15	20	30
Conversion at the gel point (%)	30 ± 0.5	3.7 ± 0.5	2.8 ± 0.5	0.9 ± 0.5	2.3 ± 0.5	1.9 ± 0.5	1.2 ± 0.5

Table III   Effect of the SiO₂ Content on the Characteristics (Time Range and Time Change) of the "Pseudoplateau" Observed on the Storage Shear Modulus vs. Reaction Time at 1 Hz for Reactive Systems Containing Different Amounts of Grafted SiO₂

SiO$_2$ (% wt)	0	5	7.5	10	15	20	30
Time width of the "rubbery plateau" (min)	—	—	11.6	20.4	36.3	44.8	—
dG'/dt (Pa/s)	—	—	2.3	3.3	5.7	13	—

where $k_{p(\mathrm{HEMA})}$ and $k_{p(\mathrm{SiO_2})}$ are the rate constants of the polymerization rate, in the bulk reacting HEMA and for the groups from the surface of the particles, respectively; and $[R^\bullet]_{\mathrm{HEMA}}$ and $[R^\bullet]_{\mathrm{SiO_2}}$ are the corresponding radical concentrations.

To calculate $v_{p(\mathrm{SiO_2})}$, v_p is reported as a function of the amount of SiO$_2$ in Figure 8. $v_{p(\mathrm{SiO_2})}$ was found to be 4.5 10^{-5} (s^{-1}), which is very low compared to that of the neat HEMA. As a consequence, the polymerization rate becomes:

$$v_p = v_{p(\mathrm{HEMA})} = k_{p(\mathrm{HEMA})} \cdot [M] \cdot [R^\bullet]_{(\mathrm{HEMA})}$$

If one supposes that the radical concentration in the filled reactive systems is the same whatever the SiO$_2$ content, the radical polymerization could be given by:

$$v_p = k_{p(\mathrm{HEMA})} \cdot \theta \cdot [R^\bullet] \cdot [M]$$

Figure 7 Transmission electron microscopy micrographs of the filled systems P(HEMA)/grafted SiO₂ with 5 wt % of SiO₂.

where $[R^\bullet]$ is the total concentration of radical, and θ is the radical fraction in the HEMA-rich domains, $[R^\bullet]_{\mathrm{HEMA}}/[R^\bullet]$.

As suggested previously, the radical concentration in the filled reactive systems could be divided to two parts: those from the HEMA phase, and the second part from the surface of the SiO₂ nanoparticles. As the radical concentration in the HEMA phase is lower than that in the case of the neat HEMA polymerization, the autoacceleration is slowed down as the SiO₂ content increases. When the radical concentration in the HEMA phase decreases, the polymerization rate at the stationary state decreases and the autoacceleration phenomena is slowed down.

CONCLUSION

The kinetic reactions and the rheological studies during the radical polymerization of the filled reactive systems demonstrate that these two phenomena are related. In the case of neat HEMA radical polymerization, the macrogelation is accompanied by the Trommosdorff effect, or gel effect, which is characteristic of radical polymerization. The addition of grafted SiO₂ nanoparticles to the HEMA monomers with a critical concentration changes the chemiorheological behavior. The macrogelation occurs even if the reactive systems are at the stationary state. The grafted SiO₂ nanoparticles react and lead to macrogelation phenomena at very low conversions compared to that of the neat HEMA reactive system. On the other hand, the polymerization rate is slow down from the presence of grafted SiO₂ nanoparticles. In fact, the polymerization rate at the surface of the grafted particles is low because of the low mobility of

Figure 8 Radical polymerization rate vs. the SiO$_2$ content in the filled reactive systems.

the methacrylate groups attached to the surface. The reactive medium could be considered as two domains. The reactive groups from the SiO$_2$ surface for which the polymerization rate is low, and those from the bulk HEMA for which the polymerization rate is the same order of magnitude as that in the case of the pure HEMA polymerization. The reduction of the mean polymerization rate is due to the reduction of the radical concentration of the neat HEMA type.

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