Inorganic−Organic Clusters of Zirconium as Initiators of Hydroxyethyl Methacrylate Polymerization

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One of the major goals in the materials field is to develop new materials having improved magnetic, optical, or catalytic properties. To this aim, hybrid polymers seem to be very promising for combining inorganic and organic components at the molecular level. This lets the composition and structures of materials be tailored through chemistry. Recently, an appealing approach has used inorganic−organic preformed or in-situ formed clusters as building blocks containing polymerizable moieties. Such oxo-clusters, based on Si, Sn, or Zr metals, were incorporated into a polymer via copolymerization with organic monomers.[1−6] Moreover, the inorganic block may also be used as both polymerization initiator or catalyst. In this sense, synthetic methods using controlled/"living" radical polymerization techniques, such as stable free-radical/nitroxide-mediated polymerizations, atom transfer radical polymerization, and reversible addition−fragmentation chain-transfer polymerization, have been already described.[7]

In a previous study,[4] the radical polymerization of 2-hydroxyethyl methacrylate (HEMA) modified by Zr(OR)$_4$ was reported. The obtained hybrid materials was constituted of nanoparticles of zirconia covalently bonded with the organic polymer network. In that case, the polymerization was initiated by dibenzoyl peroxide (4 wt %) and occurred at room temperature without any heating. The zirconium ions, complexed by acetylacetone, were proposed to catalyze the formation of radicals. In absence of acetylacetone, a soft gel was obtained. In this Communication the thermal treatments and the aging are described of a solution of Zr(OPr^n)$_4$, HEMA, and acetylacetone (1:4:0.55 molar ratio, respectively), without any typical polymerization initiator.

The differential scanning calorimetry (DSC) curve[8] recorded immediately after the mixing reagents and reported in Figure 1a shows a weak exothermal peak, with an enthalpy of about 15 J/g (see also Table 1). Also, an endothermal peak is present, due to the release of volatile species. The whole mass loss was of 41%, mainly attributable to the evolution of HEMA monomer and alcohol. Both the FTIR spectra performed on the solution, before and after the DSC, showed the peak at 1634 cm^{-1}, corresponding to the carbon−carbon double bond of HEMA (see Figure 2a,b). Zr(OPr^n)$_{4-x}$(acac)$_x$ is likely the first species formed, because of the great affinity of acacH toward transition-metal ions. Then, the reaction between the zirconium complex and HEMA occurs,[4] so that new inorganic−organic zirconium clusters, hereafter indicated as Zr(OPr^n)$_{4-x-y}$(acac)$_x$(HEMA)$_y$, are proposed to be formed "in situ".

Upon the thermal treatment at 100 °C for 3 h of the just-prepared solution, rigid monolithic bars were obtained. The DSC analysis of this treated sample, not reported, does not show any exothermal peak, and the FTIR spectrum presents the peak of C═C bonds. The flexural modulus and strength of the monoliths are 21 ± 4 MPa and 1.2 ± 0.1 MPa, respectively.[9]

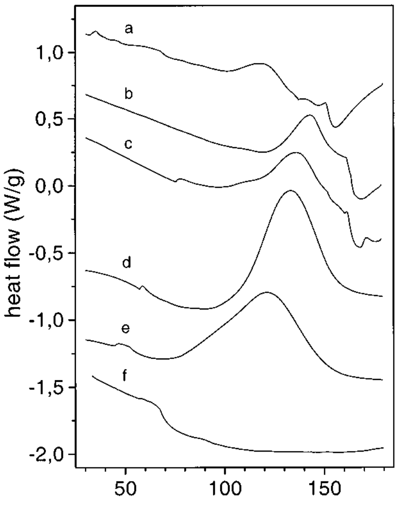

Figure 1. DSC curves of the fresh solution (a), after 24 h at 2 °C (b), after 24 h at room temperature (c), and after 48 h at room temperature (d). DSC curves of the gel formed after 48 h at room temperature: first (e) and second (f) scan.

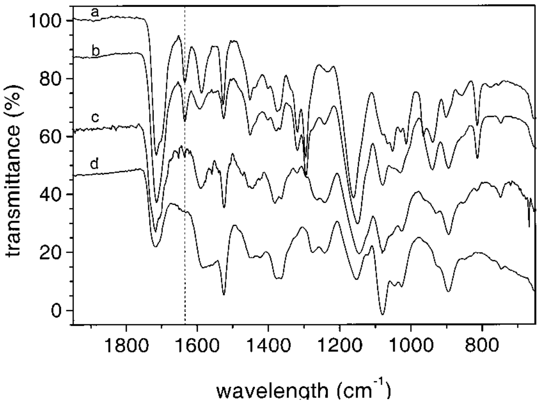

Figure 2. IR spectra of the fresh solution (a) and after DSC analyses of the fresh solution (b), of the sol (c), and of the gel (d).

Two portions of the fresh solution, left inside a closed vessel either at 2 °C and at room temperature, appeared unchanged after 24 h. However, the DSC analyses performed on them showed again an exothermal peak (see curves b and c in Figure 1), even though the intensities of the peaks are greater than before. Moreover, the mass loss recorded after these DSC analyses is lower (Table 1), suggesting that the thermal stability of the solution has been increased after 24 h. During the second run of the DSC analyses, both materials showed a glass transition in the range 50−100 °C and a further mass loss of about 7%. The IR spectra obtained from the solid residues of the DSC analyses indicated a large decrease of the peak intensity of C═C bond. To account for these findings, the polymerization of monomers should be invoked, although unexpected due to the absence of initiator. According to the IR results, only a

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Table 1

samples	T_{onset} (°C)	T_{peak} (°C)	heat of the exothermal peak (J/g)	weight loss (%)
solution as prepared	104	117	15	41
solution after 24 h at 2 °C	126	143	31	37
solution after 24 h at room temp	115	136	53	29
solution after 48 h at room temp	108	133	154	27
gel formed after 48 h at room temp	81	121	143	11

part of monomer present in the solution should have reacted, so that the solid materials exhibited a partially polymeric character.

After 48 h, the solution maintained at 2 °C was apparently unchanged, whereas a soft gel started to form at the bottom in the vessel left at room temperature, although a homogeneous liquid phase of about 20−30 vol % is still present. The study hereafter was focused on the gel and the sol formed at room temperature. The DSC analysis of both the phases was separately performed. Both the samples exhibited a very intense exothermal phenomenon, as shown in curves d and e of Figure 1, for sol and gel, respectively. The exothermal peak of the liquid phase is narrow, starting at about 100 °C with a maximum at 135 °C (Figure 1, curve d), whereas that of the gel is very broad, starting at about 70 °C with a maximum at 120 °C (see Figure 1, curve e). The reaction heat of 154 and 143 J/g was measured for the sol and the gel, respectively. The values are very close to 158 J/g, which should be the polymerization heat of the present monomer. That value is calculated on the basis of the experimental value, 290 J/g, measured for the pure monomer polymerized with BPO and assuming the whole amount of HEMA has been reacted.[4] A remarkable reduction of the mass loss (Table 1), more pronounced in the case of the gel, was also observed. To explain these findings, it should be concluded that the gel and the sol must have polymerized during DSC analysis.

The occurrence of the polymerization was confirmed by the FTIR analysis of the residues of the DSC measurements. In fact, in both the spectra reported in Figure 2, the peak at 1634 cm^{-1}, attributable to the carbon−carbon double bonds, has almost disappeared, whereas the peak of carbonyl at 1715 cm^{-1} is easily visible (see curves c and d, respectively, for the residues of the sol and gel after DSC analyses).

A semiquantitative evaluation of the percentage of reacted monomer with respect to the initial HEMA amount, R, can be considered as

$$R = 100(I_0 - I_{1634}/I_{1715})/I_0 \qquad (1)$$

where I_{1634} and I_{1715} are the intensity of the double bond and carbonyl peaks at 1634 and 1715 cm^{-1} after various treatments, respectively, and I_0 is the relative intensity of the two peaks in the initial solution. According to eq 1, the percentage of reacted monomer not only increased to 28% for the monolithic bar obtained from the solution at 100 °C for 3 h but also from 15% to about 80% after the DSC treatment of the fresh solution and samples aged for 24 h. Moreover, 85% and 93% of reacted monomer were measured for the solid residues of the DSC analyses of sol and gel, respectively, obtained after aging 48 h long at room temperature.

According to the DSC analysis (Figure 1e), 80 °C was selected as curing temperature of the formed gel. Monolithic bars were obtained after 3 h of treatment. Modulus and strength of 183 ± 10 MPa and 9 ± 1 MPa, respectively, were measured,[9] very close to $E = 223 \pm 4$ MPa and $\sigma_f = 8 \pm 5$ MPa, observed for the hybrid, with the same molar ratio derived from radical polymerization initiated by BPO (4 wt %). It should be also noted that polyHEMA polymerized by the same percentage of BPO exhibited flexural modulus and strength of 920 ± 86 MPa and 75 ± 8 MPa, respectively.

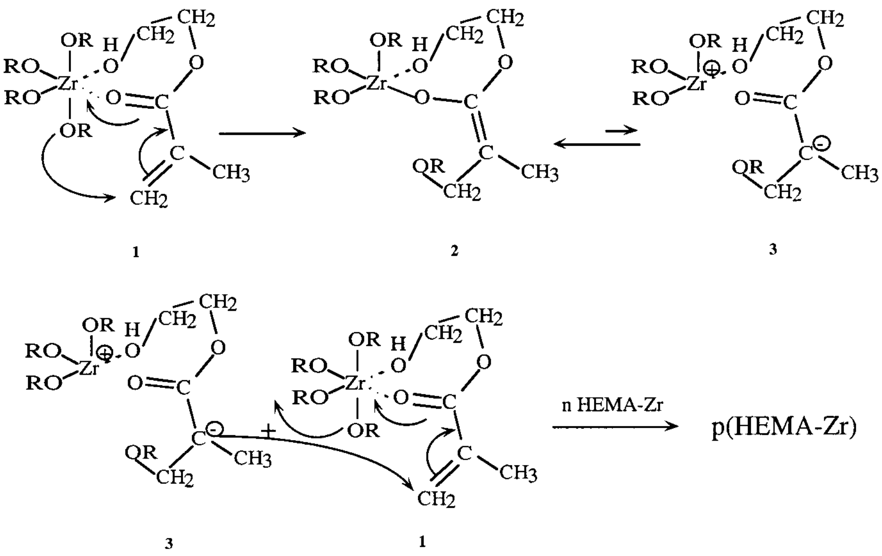
So, it could be affirmed that, whatever the mechanism of polymerization, the self-initiation should be due to the hybrid zirconium clusters. The polymerization was never observed in the same conditions for pure HEMA or for HEMA and acetylacetone. Thus, the spatial configuration of the HEMA moieties in the clusters makes the self-initiation of polymerization be easier. However, given the aging is a useful prerequisite in order to promote self-initiation, a key role is played by the aggregation of clusters or by their rearrangement.

Furthermore, a parallel experiment performed using methyl methacrylate (MMA) monomer in the same condition provided very different findings. In fact, neither gelation nor polymerization was observed in the absence of a polymerization initiator, so that in these processes the hydroxyl functionality of HEMA must play an important role. In fact, it should act like a hook to maintain the monomer in the useful regioselective orientation, reducing the possibility of a rotation of monomer. On the other hand, monolithic specimens of hybrid inorganic−organic polymer based on MMA and alkoxide of zirconium were obtained at room temperature from the solution containing BPO. Even in this last case, the metallic ions could be invoked in the initiation of radical polymerization without heating, confirming the previous results obtained for hybrid systems based on HEMA and organometallic compounds of zirconium, aluminum, and iron.[4,10]

To assess whether the self-initiation is a reliable phenomenon, many new experiments had been set up, and the preliminary results were very consistent: the self-initiation of the polymerization of the hybrid HEMA zirconium clusters in absence of BPO always occurs. The phenomenon is again observed upon increasing the molar ratio HEMA/alkoxide to 10:1, although more slowly. The kinetics seem also affected by parameters such as temperature and relative humidity, which controls the hydrolysis and condensation rate of the hybrid monomer. This indicates that small variations of the cluster structure can influence the reaction rate.

Some hypothesis can be made regarding the mechanism of the recorded self-initiation of HEMA polymerization, which must surely involve the zirconium complexes formed into the gel, as discussed before. A recent study on the polymerization of methyl methacrylate using zirconocene initiators claimed that a neutral enolate complex $Cp_2MeZrOC(OMe)C(Me)Et$ is the intermediate for propagation.[11−15] Analogously, the formation of an enolate compound is proposed in the polymerization pathway in Scheme 1. In fact, the adduct **1** of HEMA and alkoxide provides a coupling between the reagents, which is firmer than in the absence of hydroxyl, and meanwhile a favorable proximity between an alkoxide group and the carbon−carbon double bond.

Scheme 1



The transfer of an alkoxide group from zirconium ion to the C═C has a not null probability to occur, forming complex **3**. This could be responsible for propagation, reacting with **1** and eliminating an alkoxide group, which can in turn react with other complexes. The mechanism does not have to be substantially changed, even if it were adjusted to fit the oligomeric species presumably existing in the sol or gel. It explains the effect of relative humidity, which, favoring the fast hydrolysis of the alkoxide groups, reduces the probability of their transfer on the C═C and slows the initiation step. The proposed mechanism could also account for the different DSC behavior of the "ripened" gel and sol. The sol exhibits a slightly higher polymerization heat, but a greater mass loss, so that an enrichment of volatile species as propyl alcohol could be invoked.[16] The proximity of the reacting moieties in the gel results in an easier initiation, which even starts at lower temperature. In the sol the propagation is instead the faster step, due to the greater mobility of the intermediate species.

Finally, it can be concluded that a new hybrid polymer, having a molar ratio HEMA/alkoxide equal to 4, is obtained as monolith. A self-initiated polymerization of the hybrid "in-situ" formed zirconium clusters was proposed, according to a mechanism which is still to be exactly determined. So far, all the results collected indicate clearly that self-initiation of the polymerization probably occurs after a "ripening" period. The duration of the aging, necessary in order to form and rearrange the organically modified zirconium clusters, depends on temperature and relative humidity. Since the polymerization seems to occur through a coordinative and not radicalic process, a certain degree of tacticity could be expected in the organic part of polymeric hybrid. All of these results are disclosing new perspectives in the synthesis of hybrid inorganic−organic polymers.

References and Notes

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