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Retro-crosslinking of cluster-based hybrid polymers

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Abstract

Inorganic–organic hybrid polymers were prepared by co-polymerization of styrene or methyl methacrylate in the presence of small proportions of the cluster $Zr_4O_2(\text{methacrylate})_{12}$. The thermal properties of the hybrid polymers were improved by the cluster-crosslinking. Variation of the reaction conditions had little influence on the thermal properties, although the gelation times were clearly influenced. The cluster-crosslinks were completely and selectively degraded by means of acetylacetone. This allowed the unique possibility of determining the number average molecular weights and polydispersities of the organic polymers which were initially interconnected by the clusters.

Keywords: Hybrid polymer; Metal oxide clusters; Thermal properties

1. Introduction

Cluster-crosslinked polymers are a new class of inorganic–organic hybrid materials [1]. They are prepared by co-polymerization of organic monomers and inorganic clusters being substituted with polymerizable surface ligands. In own work, we are mainly using carboxylate-substituted transition metal oxo clusters as the inorganic building blocks [2]; cluster types used by other researchers to crosslink organic polymers include, for example, substituted polyoxometallates [3] and tin oxide clusters [4].

A representative example we have investigated in more detail is polystyrene (PS) or poly(methyl methacrylate) (PMMA) crosslinked by small proportions (typically <1.5 mol%) of $Zr_6O_4(OH)_4(OMc)_{12}$ (OMc = methacrylate) (**Zr6**) by free radical polymerization [5]. The obtained hybrid polymers are glassy, transparent materials which are insoluble in organic solvents but swell, the degree of swelling depending on the cluster proportion. Their properties can be traced back to an interplay between crosslinking and inorganic filler effects [6,7]. Furthermore, a stepwise polymerization protocol allowed optimizing the materials properties of the **Zr6**-based hybrid materials [8].

Due to the crosslinked structure of the hybrid polymers, polymer parameters are not accessible. An especially interesting structural aspect would be the length of the organic segments of the hybrid materials. This can be determined, if the cluster-crosslinks could be selectively degraded. While **Zr6** is rather robust and cannot be destroyed by reactions that do not affect the organic polymer, we found that another cluster, *viz.* $Zr_4O_2(OMc)_{12}$ (**Zr4**) [9,10], (Fig. 1) readily reacts with acetylacetone (acac–H) to give the soluble monomeric complex $Zr(acac)_2(OMc)_2$ (Eq. (1)) [11].

$$Zr_4O_2(OMc)_{12} + 8\text{acac–H} \rightarrow 4Zr(acac)_2(OMc)_2 + 4McOH + 2H_2O \qquad (1)$$

In this article we first describe experiments to improve the materials properties through optimization of the co-polymerization conditions of **Zr4** with styrene or methyl methacrylate. Polymerization with methyl methacrylate under non-optimized standard conditions [10] as well as the dielectric properties of the obtained hybrid polymers [12] was described previously. We then turn to the question of molecular mass distributions after degradation of **Zr4** by means of acac–H (Scheme 1) in dependence of the polymerization conditions.

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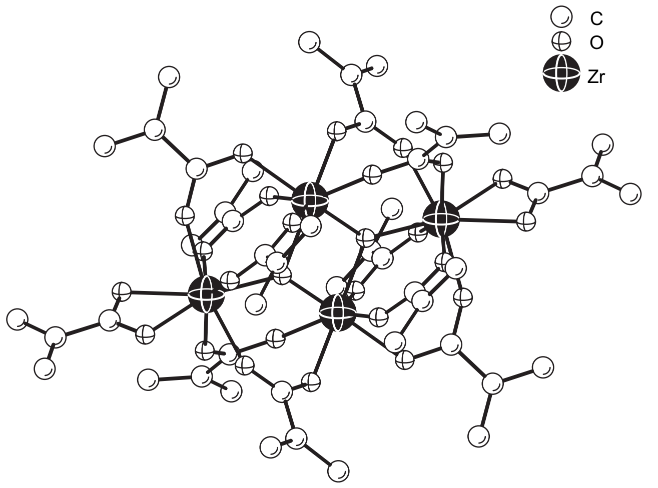
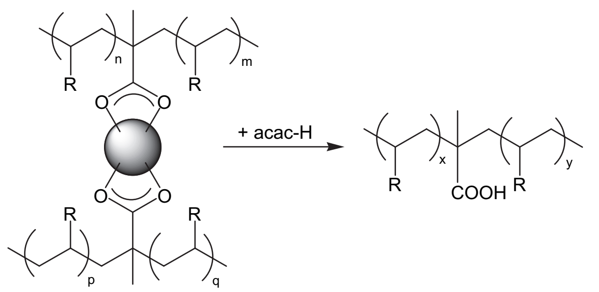


Fig. 1. Structure of $Zr_4O_2(OMc)_{12}$ (**Zr4**). A centrosymmetric (shown here) [9] and a non-centrosymmetric polymorph [10] have been found, which exhibit the same chemical behavior.



Scheme 1. Cleavage of the crosslinking **Zr4** units by acetylacetone.

Once the cluster-crosslinks were degraded, the remaining, purely organic polymer was soluble, enabling determination of polymer parameters such as number average molecular weights (M_n) and polydispersities (P_d).

2. Results and discussion

Radical-initiated co-polymerization of **Zr4** with methyl methacrylate or styrene resulted in polymers which were insoluble in ethyl acetate, THF or benzene but swelled instead.

2.1. *Zr4-crosslinked PMMA*

Polymerization of **Zr4** with methyl methacrylate as comonomer was difficult to control because of fast gel formation and auto-acceleration. This resulted in porous polymers with many bubbles. We first tried to retard the polymerization reaction and thus to prolong the gelation times by varying the initiator concentration (benzoyl peroxide, BPO) and by diluting the reaction mixtures with benzene.

First, three samples with the same composition, *viz.* ca. 1 mol% of **Zr4** dissolved in a benzene solution of methyl methacrylate, were initiated with different amounts of BPO and polymerized at 70 °C for 24 h. The methyl methacrylate to benzene wt. ratio was kept constant at 1:2.4, the smallest amount of solvent that allows complete dissolution of **Zr4**. After drying the samples *in vacuo*, the polymers were milled and extracted two times with ethyl acetate for three days each to remove benzene, followed by a repeated drying *in vacuo* at 100 °C.

Gelation times were significantly prolonged when less initiator was applied (Series A, Table 1). The polymer prepared with 0.01 wt% of BPO was obtained as a transparent bulk sample, whereas the samples prepared with 0.1 or 1 wt% initiator were porous pieces with many bubbles because auto-acceleration occurred. Typical TGA traces are shown in Fig. 2. There was a clear shift in the onset temperature of thermal decomposition for the cluster-containing samples compared with that of neat PMMA prepared and measured under the same conditions (245 °C).[1] While the gelation times were clearly influenced by the initiator concentration, there was little influence on the thermal properties (Table 1).

Pristine PMMA thermally decomposes by thermo-oxidative degradation of the polymer chains. For cluster-doped samples the behavior was different, because two additional mass loss steps were observed. The first mass loss (“mass loss 1” with the associated onset temperature “onset 1”) relates to loss of low molecular weight species such as solvent, residual monomers or oligomers. Mass loss 1 decreased from 5.1% to 3.7% by increasing the amount of initiator from 0.01% to 1%, indicating that either polymerization was more complete or that solvent removal was facilitated. Mass loss 2 originates from degradation of the main polymer chains and is the stage where char formation takes place. Onset 2 was higher when less initiator was used. Finally, the produced organic char was oxidatively volatilized at temperatures between 400 and 470 °C (mass loss 3, onset 3).

There is a correlation between crosslinking and char formation which is due to hindered degradation through unzipping of the polymer chains. When the unzipping or depropagation process reaches a crosslinking point, two or more bonds must break simultaneously to liberate a fragment. Unzipping will stop at this point for the time being since such simultaneous breaking is most improbable as long as there are other mechanisms possible [13].

In addition to TGA measurements, the samples were also characterized by DSC (Fig. 3, as an example). Onset temperatures of thermal combustion appeared at lower temperatures than found in TGA measurements because different heating rates (3 °C/min in DSC and 5 °C/min in TGA) and different atmospheres were applied (dynamic air atmosphere in TGA and static air in DSC). The DSC curve for cluster-free PMMA showed an endothermic event from 200 to 350 °C caused by chain radical reaction of depolymerization [14]. A subsequent exothermic event at higher temperatures was thus less pronounced. A different picture was observed in the cluster-crosslinked samples. Depolymerization reactions were

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[1] For one sample, LPO-catalyzed **Zr4**-crosslinked PMMA, the temperature dependence of “onset 1” on the heating rate was checked to exclude artifacts of the heating rates. It increased from 327 °C (heating rate 2 °C/min) to 341 °C (5 °C/min) and 351 °C (10 °C/min).

Table 1
Thermal data of **Zr4**-crosslinked PMMA

Sample[a]	Onset 1 [°C]	Mass loss 1 [%]	Onset 2 [°C]	Mass loss 2 [%]	Onset 3[c] [°C]	Mass loss 3 [%]	Residual mass [%]	Gelation time [min]
Series A								
0.01% BPO	165	5.1	346	79.3	442	11.6	4.0	40
0.1% BPO	162	4.0	341	78.5	447	12.5	5.0	30
1% BPO	164	3.7	338	80.8	446	9.3	4.9	7
Series B								
1:2.4[b]	162	4.0	341	78.5	447	12.5	5.0	30
1:5.2	160	4.2	340	77.9	447	10.7	6.8	38
1:10.3	153	3.1	339	83.6	442	7.6	5.4	120
Without solvent	–	–	323	–	–	–	1.1	5
Series C								
0.1% LPO, 5 min	124	5.3	337	91.4	–	7.5	2.7	30
0.1% LPO, 3 min	129	3.9	338	92.7	–	8.4	3.3	50
0.05% LPO, 5 min	122	6.2	336	90.7	–	11.9	2.7	60
0.05% LPO, 3 min	129	5.6	341	90.7	–	6.5	3.5	120

[a] SP = stepwise polymerization (see text). Series A: MMA + ca. 1 mol% **Zr4** + benzene (methyl methacrylate/benzene wt. ratio = 1:2.4). Variation of BPO concentration. Series B: MMA + ca. 1 mol% **Zr4** + 0.1 wt% BPO. Variation of methyl methacrylate/benzene ratio. Series C: MMA + 0.5 mol% **Zr4** + benzene (methyl methacrylate/benzene wt. ratio = 1:1.4). Step 1: 80 °C/3 or 5 min. Step 2: 40 °C/48 h. Step 3: 100 °C/2 h. Variation of LPO concentration and heating period of step 1. Gelation time refers to the start of the 80 °C heating period.

[b] Same as entry 2 in series A.

[c] Onset 3 cannot be determined accurately because it is strongly influenced by mass loss 2.

inhibited by incorporation of **Zr4**, and onset temperatures of thermal combustion were also shifted. The latter event took place in at least two stages, indicating again that char was formed during main polymer degradation which was then oxidatively volatilized at higher temperatures.

Next to varying the initiator concentrations, the solvent concentration was varied whereby the solvent acts for heat dissipation (Series B). Three samples with the same proportion of **Zr4** (~1 mol%) and the same amount of initiator (0.1 wt% BPO) were prepared, but with different amounts of solvent. Benzene was removed by the same protocol as before.

There was no influence of the solvent proportion on the thermal properties (Table 1). Mass losses were not different to the values obtained by initiator variation. Solely the gelation time was prolonged from 30 min for a MMA/benzene wt. ratio of 1:2.4 to 120 min for a ratio of 1:10.3. Further increase of the solvent proportion prevented gelation and the polymer was obtained as a powder.

The residual masses were higher than the theoretical values (4.2 wt%) calculated by assuming 100% polymerization yield and complete decomposition of **Zr4** to ZrO_2 during combustion. This is probably due to non-crosslinked species which were extracted by ethyl acetate, and thus increased the relative proportion of **Zr4** in the hybrid polymers.

Although most of the residual solvent was removed by the procedure described above, all materials still contained minor amounts of solvent after drying. This procedure is feasible for small polymer pieces or powders, but not for bulk samples because the solvent cannot be removed completely. Therefore, polymerization was also carried out in the absence of the solvent. However, the solubility of **Zr4** in methyl methacrylate is rather low (0.17 mol%, determined by gravimetry), and

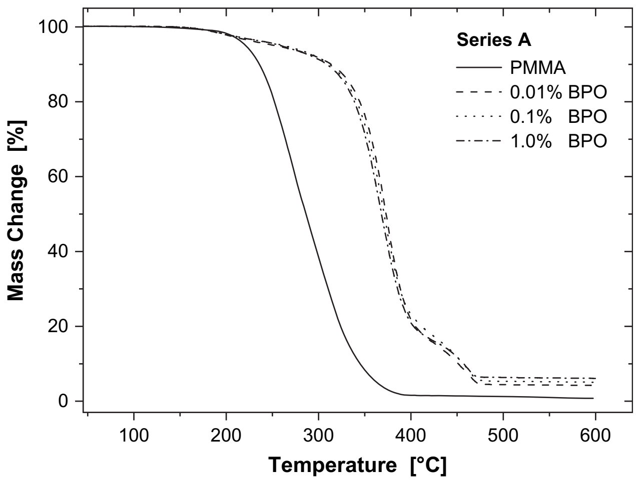

Fig. 2. TGA of PMMA crosslinked with 0.96 % of **Zr4**; variation of the initiator concentration (PMMA = cluster-free PMMA, for comparison).

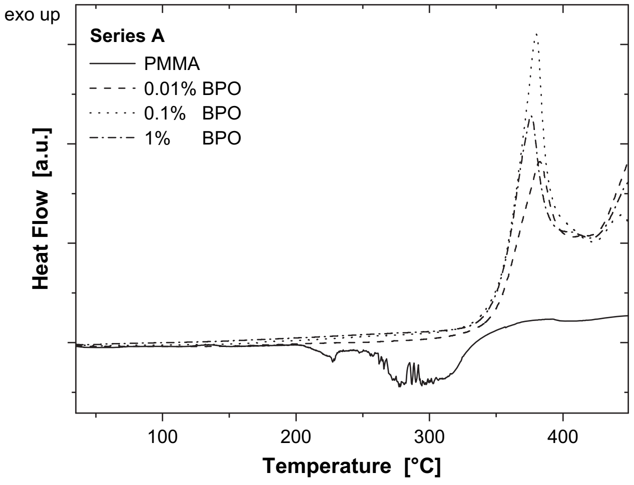

Fig. 3. DSC thermographs of **Zr4**-crosslinked PMMA; variation of initiator concentration (PMMA = cluster-free PMMA, for comparison).

therefore the cluster proportion in the hybrid polymers is distinctly lower than that in the samples prepared by polymerizing benzene solutions. Polymerization of a saturated solution of **Zr4** in methyl methacrylate was carried out by adding 1% BPO and heating to 70 °C for 24 h. The polymers were then dried *in vacuo* at 100 °C. The gelation time was very short (5 min).

The smaller proportion of **Zr4** was also reflected in thermal measurements where the first (low molecular residues) and the third (related to the cluster) mass losses were negligible. The onset temperature of thermal decomposition of the main polymer chains (Table 1) was lower when compared to the samples containing ca. 1 mol% of **Zr4**. Nevertheless, an improvement relative to the cluster-free polymer is obvious and quite remarkable when taking into account the small proportions of cluster.

A final variation of the polymerization was a stepwise polymerization protocol, which had previously led to a significant improvement of the thermal properties of PS and PMMA crosslinked by **Zr6** [8]. In this series of polymerizations (Series C, Table 1), the **Zr4** proportion was reduced to 0.5 mol% to additionally prolong the gelation times without using more solvent. Polymerization was performed in three steps: first, a benzene solution of **Zr4** and MMA was heated to 80 °C, i.e. close to the boiling point, and polymerization was started by adding lauroyl peroxide (LPO) as the initiator. The solution was kept at this temperature for 3 or 5 min, and was then immediately quenched to 0 °C in an ice-water bath. Polymerization was then continued at 40 °C for 48 h and, after removal of benzene *in vacuo*, at 100 °C for 2 h. The amount of LPO and the time of the pre-polymerization step at 80 °C were varied. The polymers were then dried as before.

The gelation times were increased by either lowering the initiator concentration or by shortening the period of the pre-polymerization step. TGA measurements (Table 1) showed a clear shift in the onset temperatures of thermal decomposition for the hybrid polymers to neat PMMA. However, there were no significant differences between the samples prepared at different conditions.

2.2. *Zr4-crosslinked PS*

The reactivity of styrene is lower than that of methyl methacrylate [15]. Therefore, different gelation times were expected upon co-polymerization with **Zr4**. The same variations of the reaction conditions were done as for the PMMA samples, and drying of the samples was performed as previously described.

First, polymerization of samples with the same **Zr4** proportion (ca. 1 mol%) dissolved in the same amount of benzene were initiated with 0.01, 0.1 or 1 wt% initiator of BPO and polymerized at 70 °C for 24 h (Series D, Table 2). Gelation times increased from 20 min for 1 wt% of initiator to 100 min for 0.01 wt% of BPO.

TGA measurements again revealed characteristic shifts of the onset temperatures of thermal decomposition due to the cluster incorporation. Since the thermal decomposition temperature of PS is 100 °C higher than that of PMMA, the relative shifts caused by cluster incorporation are small. The mass

Table 2
Thermal data of **Zr4**-crosslinked PS

Sample[a]	Onset 1 [°C]	Mass loss 1 [%]	Onset 2 [°C]	Mass loss 2 [%]	Onset 3 [°C]	Mass loss 3 [%]	Residual mass [%]	Gelation time [min]
Series D								
0.01% BPO	163	3.2	358	77.3	480	13.3	6.2	100
0.1% BPO	157	2.9	356	84.8	481	4.9	4.2	50
1% BPO	153	4.4	363	78.5	475	10.9	6.0	20
Series E								
1:2.1[b]	157	2.9	350	84.8	467	4.9	4.2	50
1:4.8	138	3.0	332	73.5	481	15.5	8.0	145
1:8.3	151	3.8	331	63.7	480	21.1	11.2	260
Without solvent	–	–	359	–	–	–	2.5	150
Series F								
2.5 min	–	2.2	319	84.4	476	9.6	3.8	135
5 min	–	2.5	322	84.4	474	9.8	3.4	110
10 min	–	1.4	328	85.0	468	7.7	6.0	90
15 min	–	3.2	323	84.0	479	9.3	3.5	70
Series G								
0.05%	–	1.2	330	82.2	472	9.6	7.1	125
0.1%[c]	–	2.5	322	84.4	474	9.8	3.4	110
0.25%	–	2.7	328	87.1	479	7.1	3.2	50
0.5%	–	4.3	335	88.0	469	4.7	2.9	40

[a] Series D: Styrene + ca.1 mol% **Zr4** + benzene (styrene/benzene wt. ratio = 1:2.1). Variation of BPO concentration. Series E: Styrene + ca. 1 mol% **Zr4** + 0.1 wt% BPO. Variation of styrene/benzene ratio. Series F: Styrene + 0.5 mol% **Zr4** + benzene (styrene/benzene wt. ratio = 1:1.45) + 0.1% LPO. Step 1: 80 °C/2.5–15 min. Step 2: 60 °C/24 h. Step 3: 80 °C/24 h + 120 °C/24 h. Variation of the heating period of step 1. Gelation time refers to the start of the 60 °C heating period. Series G: Styrene + 0.5 mol% **Zr4** + benzene (styrene/benzene wt. ratio = 1:1.45). Step 1: 80 °C/5 min. Step 2–4 as in Series F. Variation of the LPO concentration.

[b] Same as entry 2 in Series D.

[c] Same as entry 2 in Series F.

loss took place again in three stages (Table 2). The onset temperatures of thermal decomposition increased from 340 °C for pure PS by 20 °C for the cluster-crosslinked samples. Volatile compounds were released with an onset temperature of about 150–160 °C and showed a mass loss which was in the same range as in the MMA case. The third mass loss, i.e. the loss related to char volatilization, was shifted from 445 °C for the PMMA samples to about 470–480 °C in the PS samples.

TGA measurements revealed some influence of the solvent amount on thermal properties (Series E, Table 2). Mass loss 1 increased slightly with increasing amount of solvent. The onset temperatures of thermal decomposition decreased when more solvent was applied. The residual masses differed very much from the values calculated by assuming 100% polymerization conversion. This was a strong indication that polymerization was not complete when bigger amounts of solvent were applied and unreacted monomers and oligomers were removed in the extraction steps.

For higher amounts of solvent, the numerical values for the onset temperatures of thermal decomposition (Table 2) shifted to lower temperatures compared with neat PS. This is due to the different slopes of tangents in this particular region (Fig. 4). In fact, the thermal decomposition temperature was slightly improved for the hybrid polymers.

The use of solvent is apparently a crucial factor in the styrene systems. Therefore, a sample without the use of a solvent was also prepared. Unfortunately, the solubility of **Zr4** in styrene at room temperature is very small (0.08 mol%). TGA measurement (Table 2) showed little thermal shift compared to samples doped with higher cluster proportions. Nevertheless, thermal degradation was shifted by about 20 °C compared to neat PS.

A third variation was again the use of LPO as the initiator and application of a stepwise polymerization protocol. The variations were carried out in a wider range, the procedure was similar to the PMMA systems described above: a proportion of 0.5 mol% **Zr4** was dissolved in benzene, and styrene was added. After heating to 80 °C, LPO was added and the solution was kept at this temperature for 2.5–15 min. The solution was then quenched to 0 °C, and polymerization was continued at 60 °C for one day. After removal of benzene, the sample was heated to 80 °C for one day and an additional day at 120 °C. For comparison, a cluster-free sample of PS was also prepared using 0.05% of LPO and a pre-polymerization period of 5 min.

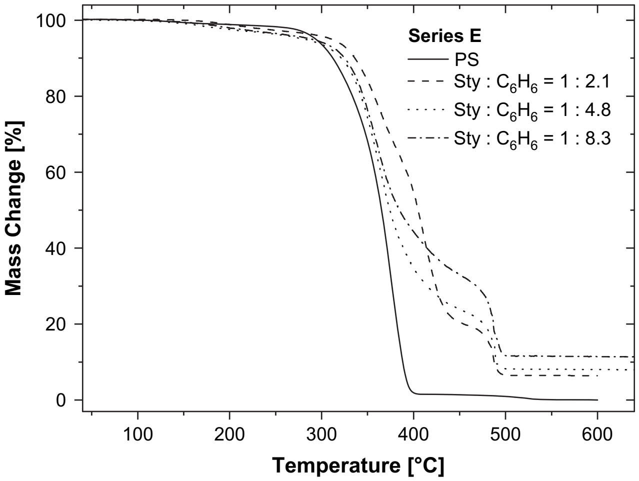

Fig. 4. TGA curves of **Zr4**-crosslinked PS samples, polymerization with solvent variation. A TGA of cluster-free PS is included for comparison.

The gelation times decreased by increasing the initial 80 °C heating period (Series F, Table 2). The thermal properties of **Zr4**-crosslinked polystyrene were not improved by this polymerization protocol. A mass loss below thermal decomposition was apparent in all hybrid polymers and was most pronounced for the sample where no pre-polymerization step was applied. Generally, the formation of char was clearer in the polystyrene case when compared to **Zr4-**crosslinked PMMA.

The initiator concentrations were also varied (Series G). To this end, the pre-polymerization period at 80 °C was kept constant at 5 min and the amount of LPO was varied between 0.05 and 0.50 wt%. Polymerization was carried out in four steps as described before.

The gelation times shortened when the initiator concentration was increased. TGA measurements revealed that an increasing amount of initiator resulted in a more pronounced mass loss below 300 °C and a smaller mass loss 3, i.e. a smaller amount of char produced in step 2. This was again rationalized by the notion that higher initiator concentrations led to hybrid polymers with higher proportions of unreacted monomers and a less degree of crosslinking.

2.3. *Degradation of the **Zr4**-crosslinked hybrid polymers by acetylacetone*

The cluster **Zr4** is degraded by acetylacetone according to Eq. (1). It was anticipated that this reaction would also take place after polymerization, i.e. that treatment with acetylacetone would destroy the cluster-crosslinks (Scheme 1). Contrary to organic crosssllinks, cluster degradation offers the unique possibility to study the molecular mass distribution of the base polymer. To this end, the milled hybrid polymers were treated with a 1:1 mixture of ethyl acetate and acetylacetone for several weeks at room temperature. Ethyl acetate was added to facilitate swelling and to dissolve the polymers after degradation of the clusters.

If degradation of **Zr4** would have stopped at the $Zr(acac)_2(OMc)_2$ stage (Eq. (1)), there was still the possibility of obtaining a polymer with zirconium atoms in the backbone because the two methacrylate ligands of $Zr(acac)_2(OMc)_2$ could as well be methacrylate groups of the cleaved polymer. Therefore, a large excess of acetylacetone was used. It was expected that the reaction would then proceed to give $Zr(acac)_4$ [16]. Furthermore, ethyl acetate and acetylacetone were not desiccated before use and thus allowed the formation of ZrO_2 by hydrolysis reactions. A colorless non-soluble, fine precipitate was indeed present in all of the samples after the degradation step, which was separated before the residual polymer was analyzed.

Table 3
Molecular weight and polydispersity of PMMA after **Zr4** degradation

Sample	M_n [kg mol^{-1}]	P_d	Gelation time [min]
1% **Zr4**, 0.01% BPO	907	4.0	40
1% **Zr4**, 0.1% BPO	388	4.4	30
1% **Zr4**, 1% BPO	105	1.9	7
1% **Zr4** + solv. 1:2.4	388	4.4	30
1% **Zr4** + solv. 1:5.2	122	2.6	38
1% **Zr4** + solv. 1:10.3	153	1.9	120
Without solvent	24	2.6	5
0.5% **Zr4**, stepwise polym. (0.1% LPO, 5 min)	87	7.6	30
0.5% **Zr4**, stepwise polym. (0.1% LPO, 3 min)	515	9.7	50
0.5% **Zr4**, stepwise polym. (0.05% LPO, 5 min)	643	2.9	60
0.5% **Zr4**, stepwise polym. (0.05% LPO, 3 min)	714	8.8	120

To verify that all Zr was removed, the polymer samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) after cluster degradation [17]. The found values were below 1 mg/g polymer; the same values were found for cluster-free PMMA and PS control samples. Thus, the **Zr4**-crosslinks of PMMA and PS were completely destroyed by reaction with acetylacetone, and the residual organic polymers were void of zirconium.

The number average molecular weights and polydispersities of the residual organic polymers determined by SEC are given in Tables 3 and 4. No clear correlation between the varied parameters (initiator concentration and amount of solvent) was observed. As a general trend, M_n and P_d were higher for longer gelation times, as expected. In the case of the PMMA samples, where the BPO concentration and the amount of solvent were varied, the polydispersities are rather large, but in an acceptable range for free radical polymerizations. For the PMMA samples prepared by the stepwise polymerization protocol, P_d was significantly larger and M_n lower, and variation of the reaction parameters had little influence. For all PS samples, the varied parameters had little influence on M_n and P_d.

Table 4
Molecular weights and polydispersities of PS after **Zr4** degradation

Sample	M_n [kg mol^{-1}]	P_d	Gelation time [min]
1% **Zr4** + solv. 0.01% BPO	43	1.8	100
1% **Zr4** + solv. 0.1% BPO	175	3.5	50
1% **Zr4** + solv. 1% BPO	97	2.3	20
1% **Zr4** + solv. 1:2.1	175	3.5	50
1% **Zr4** + solv. 1:8.3	56	1.9	260
Without solvent	22	1.8	150
0.5% **Zr4**, stepwise polym. (2.5 min)	241	3.2	135
0.5% **Zr4**, stepwise polym. (5 min)	89	5.4	110
0.5% **Zr4**, stepwise polym. (10 min)	102	4.4	90
0.5% **Zr4**, stepwise polym. (15 min)	78	5.2	70
0.5% **Zr4**, stepwise polym. (0.05% LPO)	394	2.6	125
0.5% **Zr4**, stepwise polym. (0.1% LPO)	89	5.4	110
0.5% **Zr4**, stepwise polym. (0.25% LPO)	90	4.1	50
0.5% **Zr4**, stepwise polym. (0.5% LPO)	66	3.7	40

3. Conclusions

The use of the **Zr4** cluster as a crosslinking co-monomer in polymerization reactions of methyl methacrylate or styrene resulted in hybrid materials which generally showed improved thermal properties when compared to the cluster-free polymers. In the case of crosslinked PMMA also depolymerization reactions were inhibited. The main problem in the preparation of the **Zr4**-crosslinked hybrid polymers was the short gelation times due to crosslinking of the multifunctional cluster. Short gelation times resulted in porous materials with many bubbles. However, glassy, transparent bulk polymer samples were obtained through prolonging the gelation times by either reducing the amount of the initiator BPO or by adding more solvent to the polymerization solution. Alternatively, the initiator LPO was used and a stepwise polymerization protocol was applied. The gelation times were controlled by varying the amount of initiator and by reducing the time of the pre-polymerization period.

While the gelation time, and thus the appearance of the hybrid polymers, was clearly influenced by variations of the reaction conditions, there was small to no influence on the thermal properties. For **Zr6**-crosslinked hybrid polymers, we had previously obtained remarkable improvements in thermal properties by properly adjusting the polymerization conditions, especially by lowering the initiator activity and by applying a stepwise polymerization protocol, thus avoiding auto-acceleration [8]. This was not the case for the **Zr4**-crosslinked polymers. These observations can be explained by the influence of the (inorganic) cluster core on the reactivity of the methacrylate ligands on the cluster surface. The reactivity of the methacrylate ligands of **Zr4** obviously is in a range that ‘‘standard’’ polymerization conditions are already close to optimal and variation of the polymerization conditions only results in minor improvements.

The fact that the crosslinking **Zr4** cluster units can be selectively and completely degraded with acetylacetone offered the unique possibility to study M_n and P_d of the organic constituents of the hybrid polymers. Atomic emission spectroscopy investigations confirmed that all of the **Zr4** units were completely destroyed. The released polymer chains were characterized by SEC and showed large polydispersities. Hild et al. investigated the network formation in free radical co-polymerizations of styrene with bi-unsaturated co-monomers such as divinylbenzene and ethylene dimethacrylate in detail [18]. They found that shortly after the gel point a considerably high proportion of the macromolecules was not yet connected to the network. By extracting these non-linked polymers they made a rough investigation of M_n and P_d. In early stages of gelation, the polydispersity of the extracted polymers was quite high ($\sim$4.5) but decreased by time with concomitant increase of molecular weight. They concluded that pendent double bonds attached to these species were potential linking points and that the probability of bond formation increased with higher average molecular mass of the polymers. Similar considerations may apply to the cluster-crosslinked polymers, i.e. in early stages only one methacrylate group of **Zr4** is attached to a growing polymer chain and a second, third, etc. double bond was consumed at higher rates of conversion.

4. Experimental section

Thermal Gravimetric Analyses (TGA) were carried out on a Netzsch TG209C, with a heating rate of 5 °C/min in synthetic air atmosphere at a flow rate of 30 ml/min. Temperature calibration was performed using standard calibration sets. DSC measurements were performed on a Shimadzu DSC-50 differential scanning calorimeter at a heating rate of 3 °C/min in static air atmosphere. A Spectro ICP-OES model Spectroflame P was used for the measurement of the Zr samples at 343.823 nm. The free running radiofrequency generator operating at 27.5 MHz was used at an output power of 5 kW at maximum (coolant argon flow rate 14 l/min, auxiliary argon 1 l/min, nebulizer argon gas flow 1 l/min). Size exclusion chromatography (SEC) was performed in THF using a Waters system including a 515 HPLC pump, a 717 autosampler, a 2410 differential refractive index detector and Styragel columns (HR 0.5, 3 and 4, linear and GPC phase SDV 50/100/10E5A) at 40 °C at a rate of 1 ml/min applying linear polystyrene standards.

Zr4 is water-sensitive. Therefore, the monomers as well as the used solvents were carefully desiccated. Methyl methacrylate was distilled twice from CaH_2 to remove both inhibitors and water. $Zr_4O_2(OMc)_{12}$ (**Zr4**) was prepared as previously described [9].

4.1. Preparation of cluster-free PMMA (for comparison)

An amount of 22.3 mg of BPO was added to 2.130 g (21.28 mmol) of methyl methacrylate, and polymerization was carried out at 70 °C for 24 h. The sample was then dried *in vacuo*.

4.2. Preparation of $Zr_4O_2(OMc)_{12}$-crosslinked PMMA

4.2.1. Variation of the initiator proportion

An amount of 558 mg (0.39 mmol) of **Zr4** was dissolved in 9.8 g of benzene. After addition of 4.067 g (40.63 mmol) of methyl methacrylate, 0.01 wt%, 0.1 wt% or 1.0 wt% of BPO were added to aliquots of this solution. The samples were polymerized at 70 °C for 24 h. After removal of the solvent *in vacuo*, the polymers were milled and twice swollen in ethyl acetate for 3 days each and then dried *in vacuo* at 100 °C.

4.2.2. Variation of the solvent proportion

An amount of 105 mg (0.074 mmol) of **Zr4** was dissolved in 7.458 g of benzene. After addition of 724 mg (7.23 mmol) of methyl methacrylate (MMA/benzene wt. ratio 10.1), the solution was heated to 70 °C, and polymerization was started by the addition of 0.7 mg of BPO. The sample was heated to 70 °C for 1 day, and benzene was then removed *in vacuo*. The solvent was removed by the same procedure as above. Samples with a MMA/benzene wt. ratio of 5.2 and 2.4 were accordingly prepared.

4.2.3. Polymerization without solvent

An amount of 5.029 g of methyl methacrylate was added to 517 mg of **Zr4**. The mixture was stirred at room temperature for 15 min after which the non-dissolved **Zr4** was allowed to sediment (469 mg after drying). An amount of 2 ml of the clear solution was polymerized at 70 °C by initiating with 2.1 mg of BPO. After 24 h, the sample was dried *in vacuo*.

4.2.4. Stepwise polymerization

An amount of 252 mg (0.178 mmol) of **Zr4** was dissolved in 5.008 g of benzene. After addition of 3.55 g (35.46 mmol) of methyl methacrylate, the solution was heated to 80 °C and polymerization was initiated by the addition of 3.5 mg of LPO. The sample was kept at 80 °C for 3 min. The flask was then quenched in an ice-water bath to 0 °C. Polymerization was then carried out at 40 °C for 48 h. After removal of the solvent *in vacuo*, the temperature was raised to 100 °C for 2 h. The solvent was removed by the same procedure as above. Samples with 0.05 wt% LPO and/or 5 min pre-polymerization periods were prepared accordingly.

The reference sample of PMMA without cluster was prepared with 0.1 wt% LPO and a pre-polymerization period of 3 min under otherwise identical conditions. The sample was not treated with ethyl acetate.

4.3. Preparation of cluster-free PS (for comparison)

An amount of 36.7 mg of BPO was added to 3.879 g (37.24 mmol) of styrene. Polymerization was carried out at 70 °C for 24 h. The sample was then dried *in vacuo*.

4.4. Preparation of $Zr_4O_2(OMc)_{12}$-crosslinked PS

4.4.1. Variation of the initiator proportion

An amount of 132 mg (0.093 mmol) of **Zr4** was dissolved in 2.027 g of benzene and 0.977 g (9.38 mmol) of styrene was added, followed by heating to 70 °C. Polymerization was initiated by adding 1.1 mg of BPO. The sample was polymerized at 70 °C for 24 h. After removal of the solvent *in vacuo*, the polymer was swollen twice in ethyl acetate for 3 days each and then dried *in vacuo*. The solvent was removed by the same procedure as above. Samples with 1% and 0.01% of BPO were accordingly prepared.

4.4.2. Variation of the solvent proportion

An amount of 152 mg (0.107 mmol) of **Zr4** was dissolved in 5.536 g of benzene, and 1.162 g (11.16 mmol) of styrene was added, followed by heating to 70 °C. Polymerization was initiated by adding 1.2 mg of BPO, the sample was then polymerized at 70 °C for 24 h. The solvent was removed by the same procedure as above. Samples with solvent/monomer ratios of 1:2.1 and 1:8.3 were accordingly prepared.

4.4.3. Polymerization without solvent

An amount of 4.311 g (41.39 mmol) of styrene was added to an amount of 322 mg (0.227 mmol) of **Zr4**. The solution was stirred at room temperature for 15 min, and non-dissolved **Zr4** (275 mg after drying) was allowed to sediment. An amount of 2 ml of the clear solution was polymerized at 70 °C by initiating with 1.9 mg of BPO. After 24 h, the sample was dried *in vacuo*.

4.4.4. Stepwise polymerization

An amount of 223 mg (0.157 mmol) of **Zr4** was dissolved in 4.746 g of benzene. After addition of 3.270 g (31.40 mmol) of styrene, the solution was heated to 80 °C, and polymerization was initiated by the addition of 3.2 mg of LPO. The sample was kept at 80 °C for 3 min. The flask was then quenched in an ice-water bath to 0 °C. Polymerization was carried out at 60 °C for 24 h. After removing the solvent *in vacuo*, the temperature was raised to 80 °C for 24 h and post-polymerization was carried out at 120 °C for another 24 h. The sample was then dried *in vacuo*. The solvent was removed by the same procedure as above. Samples with different pre-polymerization periods or initiator concentrations were prepared correspondingly.

4.5. Treatment of the hybrid polymers with acetylacetone

An amount of 100 mg of milled **Zr4**-crosslinked PMMA or PS was put into a mixture of 5 ml of acetylacetone and 5 ml of ethyl acetate. Depending on the grain size of the polymer, the solution was stirred up to two months. The viscous solution was then precipitated in a 30-fold excess of methanol. The polymer was separated by decanting the solution or by centrifugation. The solid was re-dissolved in ethyl acetate by stirring for a few hours, and the non-soluble precipitate was centrifuged off. The precipitation/re-dissolving step was repeated twice; the sample was then dried *in vacuo* and dissolved in THF for SEC measurements.

4.5.1. Determination of residual Zr

Polymer samples were weighed into Duran glass liners and heated to 550 °C in air with a heating rate of 5 °C/min. The maximum temperature was maintained for 1 h. The residue, consisting of ZrO_2, was then washed out of the liners successively with 2.5 ml of conc. HCl, 2 ml of conc. HNO_3 and 0.5 ml of conc. HF.

The acid fractions were combined in PTFE vessels for microwave digestion using a Multiwave 3000 pressurized microwave digestion system (Paar, Graz, Austria). A ramp was applied from 0 to 1400 W in 7 min. The mixture was then held for 23 min ($p_{\max}$ 20 bar, $T_{\max}$ 180 °C). After cooling to room temperature, the solutions were transferred into smaller PTFE vessels. The vessels were washed several times with bidistilled water. The washing and the sample solutions were combined, and 100 μl of perchloric acid was added. After evaporating the volatiles overnight in an aluminum heating block, 1.5 ml of aqua regia was added, and the solution was heated to 105 °C. By increasing the temperature to 150 °C, the volatiles were removed until a perchloric acid bead remained. The bead was dissolved in 4 ml of 5% HCl and filled up to 10 g with bidistilled water.

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