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Crosslinking vs. filler effect of carboxylate-substituted zirconium oxo clusters on the thermal stability of polystyrene

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Abstract

Inorganic–organic hybrid materials were prepared by step-wise free radical polymerization of styrene in the presence of zirconium oxo clusters of the general compositions $Zr_6O_4(OH)_4(\text{carboxylate})_{12}$ (carboxylate = 5-norbornene-2-carboxylate or isobutyrate/methacrylate) and $Zr_{12}O_8(OH)_8(\text{carboxylate})_{24}$ (carboxylate = acetate/propionate, vinylacetate, or acetate/methacrylate). Clusters with non-polymerizable ligands resulted in cluster/polystyrene blends which were soluble in toluene, whereas clusters with polymerizable ligands gave cluster-crosslinked, swellable polymers for which solvent uptake correlated with the functionality of the corresponding cluster. The onset temperatures of thermal decomposition and the glass transition temperatures of all cluster-containing polymers were higher than that of neat polystyrene, independent of whether the clusters were crosslinking or blended into the polymer.

Keywords: Metal oxide clusters; Hybrid polymer; Thermal properties

1. Introduction

Inorganic–organic hybrid materials have attracted much attention because of their high potential as tailor-made, advanced materials [1]. In class II hybrid materials, the inorganic and organic constituents are connected by strong chemical bonds, while in class I materials the inorganic entities are physically entrapped in an organic polymer matrix, or, *vice versa*, organic compounds in an inorganic matrix. A sub-class of polymeric hybrid materials is obtained when inorganic clusters are employed as the inorganic constituents [2]. Clusters offer some advantages due to their small, tunable, well defined size and shape, and because of the ease of a chemical surface modification. Moreover, the metal cluster may have intrinsic (e.g., optical or magnetical) properties [1,3].

Several types of transition metal oxo clusters were used to prepare class II hybrid polymers; this requires the presence of polymerizable ligands at the cluster surface. The organofunctional clusters are then polymerized in the presence of organic co-monomers. For example, we have prepared cluster-crosslinked inorganic–organic hybrid polymers by free radical or ring-opening metathesis polymerization of carboxylate-substituted metal oxo clusters $M_aO_b(OH/OR)_c(OOCR')_d$ or $M_aO_b(OOCR')_d$, where M = Ti, Zr, Hf, Ta, Y, etc. and R′ represents a polymerizable group, with acrylates, styrene or norbornadiene as co-monomers [4,5]. The preparation of cluster-crosslinked bulk polymer samples requires accurate control over the polymerization process to obtain homogeneous materials [6].

Little work has been performed with clusters as nanofillers in class I materials. Unlike pure inorganic fillers, such as inorganic particles, carbon nanotubes or exfoliated clays, the organic groups at the cluster surface provide a better compatibility with organic polymers or monomers. The most closely related materials are polymers reinforced with polyhedral oligomeric silsesquioxanes (POSS), $[RSiO_{3/2}]_n$. Inorganic–organic hybrid materials can be obtained by incorporating POSS molecules into polymers by copolymerization, grafting

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or blending [7,8]. While the thermal properties of polymers with pending or crosslinking POSS molecules were extensively investigated, comparatively little work was done on dispersions of non-functional POSS in polymers [9–11], i.e., where the POSS molecules are nanofillers [8].

The materials prepared by polymerization of carboxylate-substituted metal oxo clusters with organic co-monomers showed improved thermal and mechanical properties compared to the cluster-free polymers [5,6,12,13]. Although swelling experiments clearly showed that the organic polymers are crosslinked by the multifunctional clusters, it cannot be excluded that the cluster-influence on the materials' properties is partly due to nanofiller effects. For example, the thermo-oxidative stability of polypropylene was reported to be strongly improved by incorporation of untethered metal-containing POSS molecules [9]. Thus, we prepared polystyrene-based hybrid polymers either by copolymerization of functional clusters or by blending non-polymerizable clusters. In the latter case the clusters are only embedded in the polymer and thus can only act as nanofillers, while in the former case the clusters are part of the network and crosslink the polymer. In this work, we discuss how this difference influences the thermal stability of the hybrid materials.

2. Experimental

Crystalline clusters of the type $Zr_6O_4(OH)_4(carboxylate)_{12}$ (Zr_6) and $Zr_{12}O_8(OH)_8(carboxylate)_{24}$ (Zr_{12}) were prepared by controlled hydrolysis and condensation reactions of $Zr(OBu)_4$ (80% in BuOH) in the presence of the corresponding carboxylic acid as previously described [4,5,14,15]. The clusters used in this work are $Zr_{12}O_8(OH)_8(OOCMe)_{24}\cdot 6MeCOOH$ (**Zr12Ac**), $Zr_{12}O_8(OH)_8(OOCEt)_{24}\cdot 6EtCOOH$ (**Zr12Prop**), $Zr_{12}O_8(OH)_8(OOCMe)_{16}(OOCCMe{=}CH_2)_8\cdot 6MeCOOH$ (**Zr12AcMc**), $Zr_{12}O_8(OH)_8(OOCCH_2CH{=}CH_2)_{24}\cdot 6CH_2{=}CHCH_2COOH$ (**Zr12Vin**), $Zr_6O_4(OH)_4(OOCCMe{=}CH_2)_{12}\cdot 3CH_2{=}CMeCOOH$ (**Zr6Mc**), $Zr_6O_4(OH)_4$(*endo*-, *exo*-OOC–Norb)$_{12}\cdot$ 3*endo*-, *exo*-OOC–Norb (**Zr6Norb**) (Norb = norbornenyl) and $Zr_6O_4(OH)_4(OOCCHMe_2)_4(OOCCMe{=}CH_2)_8(BuOH)\cdot 4RCOOH$ ($R = CH_2Me$ or $CMe{=}CH_2$) (**Zr6IbMc**).

2.1. Polymerization reactions

Neat polystyrene (**PS**) and the hybrid polymers were prepared (Table 1) by slight modification of the previously reported step-wise free radical polymerization procedure [6] using standard Schlenk technique under dry Ar atmosphere. Lauroyl peroxide (LPO, Acros, 99%) was used as-received. Styrene (Aldrich, 99%) was distilled once, dried with CaH_2, and distilled again prior to use. Cluster-containing hybrid polymers are labeled as **PS–YY** where **YY** is the cluster acronym.

Preparation of the sample **PS–Zr12Ac** is given as an example: An amount of 2.3 mg of lauroyl peroxide was added to a solution of 559 mg (178 μmol) of **Zr12Ac** in 4.545 g (43.64 mmol) of styrene. The solution was kept at 80 °C for 3 min and then quenched to 0 °C in an ice-water bath. Polymerization was carried out at 60 °C for 24 h, post-polymerization at 120 °C for another 24 h. The sample was then dried *in vacuo* at 120 °C.

2.2. Characterization

Thermal gravimetric analysis (TGA) was carried out on a Netzsch TG209C with a heating rate of 5 °C/min in flowing synthetic air (30 ml/min). Differential scanning calorimetry (DSC) of powdered polymer samples was performed on a Shimadzu DSC-50 in air with a heating rate of 3 °C/min. Glass transition temperatures (T_g) were determined from the second heating scan at a heating rate of 40 °C/min by taking the onset temperature (the point of intersection of the tangent drawn at the point of greatest slope with the extrapolated baseline) of the thermal event.

Size exclusion chromatography (SEC) was performed in tetrahydrofuran (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. Non-crosslinked samples were dissolved in ethyl acetate and filtered. After concentrating the filtrate, the polymer was precipitated by adding the filtrate dropwise to methanol, filtered off, dried and redissolved in THF for SEC. Molecular weight analysis was carried out using Waters Millennium software including the GPC/V option and related to an internal standard (diphenyl ether).

For determination of the *degree of swelling*, the crosslinked hybrid polymers were swollen in ethyl acetate, washed with ethyl acetate to remove unreacted species and dried *in vacuo* at 120 °C. This procedure was repeated once. Pre-weighed

Table 1
Preparation of cluster-doped polystyrene samples

Sample	Cluster [mg/μmol]	Styrene [g/mmol]	Cluster proportion [mol%]	LPO [mg]	Appearance of the polymerized samples
PS	–	4.545/43.64	–	2.3	Clear
PS–Zr12Ac	559/178	4.545/43.64	0.41	2.3	Turbid
PS–Zr12Prop	664/212	4.545/43.64	0.48	2.2	Turbid
PS–Zr12AcMc	719/215	4.545/43.64	0.49	2.1	Clear
PS–Zr12Vin	751/192	4.545/43.64	0.44	2.8	Clear with bubbles
PS–Zr6Norb	597/218	4.545/43.64	0.50	2.3	Turbid, few bubbles
PS–Zr6IbMc	467/219	4.545/43.64	0.50	2.2	Clear

LPO = lauroyl peroxide.

polymer pieces were then stored in toluene at 25 °C, and the mass was determined in 24 h intervals. Once no further solvent uptake was observed, the degree of swelling, d_{sw}, was determined according to the following equation:

$$d_{sw} = \frac{m_{sw} - m_{dry}}{m_{dry}} \cdot 100\%$$

where m_{sw} and m_{dry} is the mass of the polymer in the swollen and in the dry state, respectively.

FTIR spectra of powdered polymer samples were recorded on a Bruker Tensor 27 spectrometer in transmission mode from 4000 to 450 cm^{-1} using KBr pellets.

3. Results and discussion

3.1. Polymerization

Three different cluster types were employed for the preparation of the polystyrene hybrid polymers:

(1) Clusters with methacrylate ligands which were previously shown to react with styrene as co-monomer in free radical polymerizations to give cluster-crosslinked polystyrene. Both **Zr6IbMc** and **Zr12AcMc** contain eight methacrylate ligands.
(2) Clusters with ligands which are less prone to free radical polymerizations. The clusters **Zr6Norb** and **Zr12Vin** thus constitute intermediate cases between (1) and (3).
(3) Clusters without polymerizable ligands: the clusters **Zr12Ac** and **Zr12Prop** cannot be connected to the polymer matrix by covalent bonds and thus do not contribute to network formation.

The structures of the clusters employed in this work (Fig. 1) were discussed in detail elsewhere. It was also shown that the Zr_6 and Zr_{12} clusters, despite their structural similarity, are not convertible in solution [14,15].

The polymerization protocol applied for the preparation of the cluster-doped polystyrene in this work was originally developed for the preparation of **PS–Zr6Mc** and allowed the synthesis of defect-free hybrid samples with cluster loadings up to 0.87 mol% on a large scale without running into the problems of auto-acceleration during polymerization [6,12]. The clusters were dissolved in styrene and pre-polymerization was initiated by small proportions of lauroyl peroxide at 80 °C for a short time. After quenching the reaction by cooling at 0 °C, the solutions were polymerized at 60 °C and then at 120 °C. A cluster proportion of 0.4–0.5 mol% was chosen because this was shown to be an optimum concentration with regard to the thermal properties of the hybrid polymers.

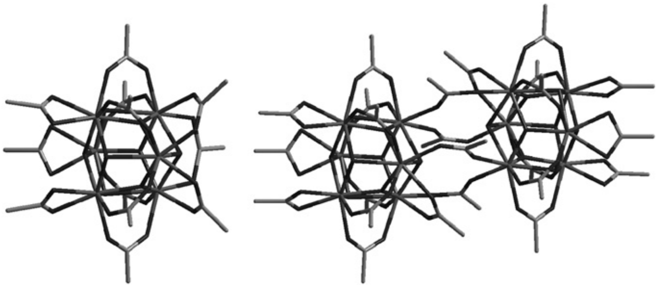

Fig. 1. General structures of the clusters $Zr_6O_4(OH)_4(carboxylate)_{12}$ (Zr_6) and $Zr_{12}O_8(OH)_8(carboxylate)_{24}$ (Zr_{12}).

The Zr_6 clusters **Zr6Norb** and **Zr6IbMc** were sufficiently soluble in styrene at room temperature; the concentration in the starting solution was 119 mg cluster/ml styrene, and 93 mg cluster/ml, respectively. A series of **PS–Zr6Mc** samples with varying cluster proportions was reported elsewhere [12]; the sample **PS–Zr6Mc** with 0.43 mol% cluster (74 mg cluster/ml styrene) is included in the discussion for comparison. The Zr_{12} clusters were less soluble in styrene because of the higher molecular mass and the different ligands. The employed cluster concentrations in the starting solutions (**PS–Zr12Ac** 112 mg/ml, **PS–Zr12Prop** 133 mg/ml, **PS–Zr12Vin** 150 mg/ml, **PS–Zr12AcMc** 144 mg/ml) corresponded to the maximum solubility in styrene at room temperature.

In the absence of clusters, styrene gelled after ca. 4 h under the applied polymerization conditions (gelation time = time from the start of the 60 °C heating period till gelation). The gelation times (Table 2) were shortened to 160 min or 190 min in the presence of **Zr12Ac** or **Zr12Prop**. The resulting hybrid materials **PS–Zr12Ac** and **PS–Zr12Prop** were whitish, indicating some phase separation. Phase separation on different length scales is a general problem in cluster/polymer systems and has been investigated by SAXS and TEM for different systems [16]. Gelation times were considerably shortened with **Zr6IbMc** and **Zr12AcMc** as expected for crosslinked samples, e.g., the **PS–Zr6Mc** had a gelation time of 65 min. Clear, transparent polymers were obtained.

When styrene was polymerized in the presence of **Zr12Vin** with allylic ligands, gelation did not happen within 24 h at 60 °C. After increasing the temperature to 120 °C, auto-acceleration occurred and a clear polymer with many bubbles was obtained. The absence of gelation during the 60 °C period is explained by the lower reaction rates of allylic compounds which results in oligomeric products because of degradative chain transfer to the monomer during radical polymerization [17]. Gelation time in the polymerization of **Zr6Norb** with styrene was 190 min and a turbid polymer with a few bubbles was obtained. It has been reported that increased temperatures

Table 2
Gelation times, swelling and SEC data of the hybrid polymers

Sample	Gelation time	Degree of swelling [%]	M_n [kg mol^{-1}]	P_d
PS	>4 h	–	181.1	6.6
PS–Zr12Ac	160 min	–	137.4	5.9
PS–Zr12Prop	190 min	–	362.4	10.0
PS–Zr12AcMc	50 min	231	–	–
PS–Zr12Vin	>24 h	–	385.7	6.6
PS–Zr6Norb	190 min	–	279.8	7.0
PS–Zr6IbMc	60 min	318	–	–
PS–Zr6Mc	65 min	243	–	–

M_n = number molecular weight, P_d = polydispersity.

are necessary to obtain high yields when norbornene compounds are polymerized [18].

3.2. Characterization

Previous investigations have shown that the integrity of the clusters is preserved upon polymerization [19]. Characterization of the hybrid polymers in this work was therefore restricted to a qualitative check of unreacted double bonds by FTIR spectroscopy. It should be pointed out that an individual optimization of the polymerization conditions for the various samples was not intended in this work. Only three FTIR spectra (of **PS–Zr6IbMc**, **PS–Zr12Prop** and **PS–Zr12Vin**) are shown in Fig. 2, representing the three different cluster types. The presence of a band at ~1645 cm^{-1} (C=C stretching vibration) in **PS–Zr12Vin** indicates unreacted double bonds due to incomplete polymerization. Very weak bands were observed for the samples **PS–Zr6IbMc** and **PS–Zr6Norb**, and the band was absent in the other samples (not shown).

Samples **PS–Zr12Ac**, **PS–Zr12Prop**, **PS–Zr12Vin** and **PS–Zr6Norb** were readily dissolved in ethyl acetate. This shows that the unsaturated groups of vinylacetate and norbornenyl carboxylate were not reactive enough to crossslink the polystyrene chains at all or to a sufficient degree. The polymer solutions were subjected to size exclusion chromatography (Table 2). There was no clear correlation between t_{gel} and M_n because of the different carboxylate ligands of the clusters and because there is no information whether or to what extent the clusters interact with the polymers, e.g., via the μ_3-OH groups. The polydispersities (P_d) of the polymers were high in each sample.

Hybrid polymers crosslinked with various proportions of the cluster **Zr6Mc** showed solvent uptake which correlated with the cluster proportion, i.e., the crosslinking density [12,20]. For example, the sample crosslinked with 0.43 mol% of **Zr6Mc** showed a degree of swelling, d_{sw}, in toluene of 244%. This corresponds to crosslinking **PS** with about 0.5 mol% of divinylbenzene [21]. Samples **PS–Zr12AcMc** and **PS–Zr6IbMc** were both crosslinked with clusters carrying eight reactive methacrylate units each. The different solvent uptake (Table 2) might be a consequence of the different structures of the clusters.

TGA of the cluster-doped polystyrene samples in air showed that the total mass loss occurred in three stages (Fig. 3, Table 3). Mass loss 1 with onset temperature 1 was ascribed to the volatilization of low molecular weight species such as unreacted monomer or small oligomers. This mass loss is relatively low in the crosslinked samples **PS–Zr6IbMc** and **PS–Zr12AcMc** which is a proof for the efficiency of the step-wise polymerization procedure for the crosslinked systems. Mass loss 1 was higher in all other samples prepared with less reactive or non-functional Zr_6 and Zr_{12} clusters.

Degradation of the main polymer chains is characterized by mass loss 2 and onset 2. The onset temperatures showed that thermal degradation was shifted to higher values for all cluster-containing samples relative to neat **PS**. Remarkably, the shifts in the non-crosslinked samples (**PS–Zr12Ac** and **PS–Zr12Prop**) were of the same order as it was for the crosslinked samples (**PS–Zr6IbMc** and **PS–Zr12AcMc**). The onset temperatures of the non-crosslinked samples were even somewhat higher compared to the crosslinked polymers. However, these values have to be taken with caution, because the tangent, drawn at the extrapolated baseline of the TGA curve, is strongly influenced by onset 1 as well as by a different slope during the degradation step. Onset 2 of **PS–Zr6Norb** is formally too high (sharp decline) and onset 2 of **PS–Zr12AcMc** is too low (flat decline).

Mass loss 3 describes the volatilization of organic char produced during the main degradation process. Char formation depends on both crosslinking and addition of inorganic fillers. For example, it has been shown that thermal degradation of

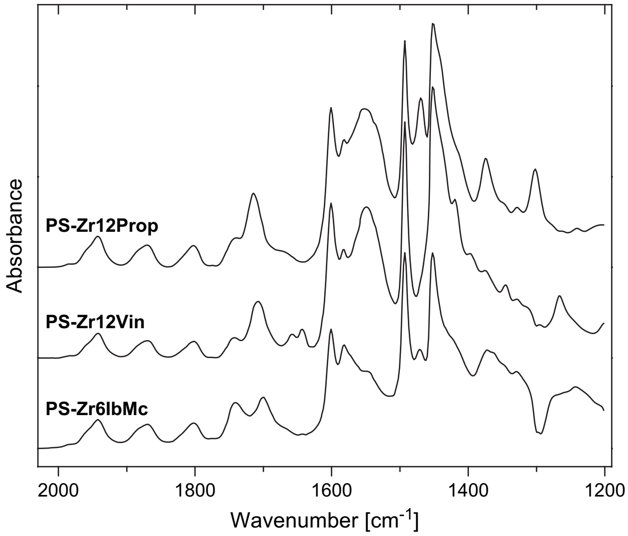

Fig. 2. Sections of the FTIR spectra of **PS–Zr12Prop**, **PS–Zr12Vin** and **PS–Zr6IbMc**; the vertical axis was shifted for clarity.

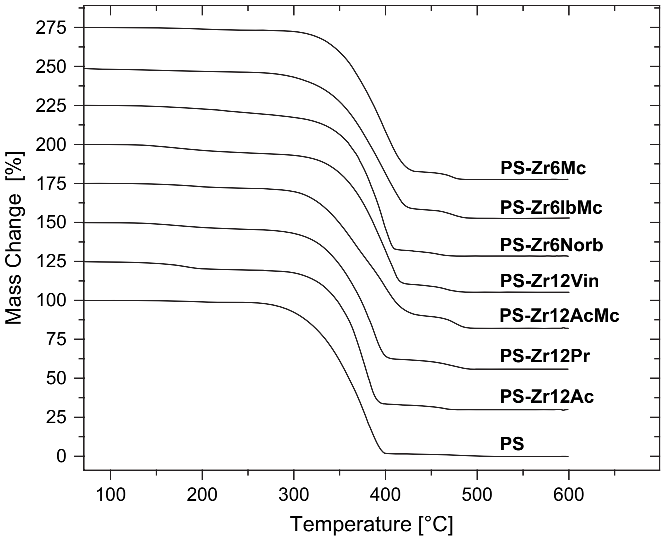

Fig. 3. TGA curves of the cluster-doped hybrid polymers in air. Pristine **PS** is shown as a reference. Each curve is shifted on the vertical axis by 25% relative to the previous curve for clarity.

Table 3
TGA and DSC results of the cluster-doped **PS** samples in air

Sample	Onset 1 [°C]	Mass loss 1 [%]	Onset 2 [°C]	Mass loss 2 [%]	Onset 3 [°C]	Mass loss 3 [%]	Residual mass [%]	T_g [°C]
PS	148	1.8	321	96.4	473	2.0	0	100
PS–Zr12Ac	155	5.5	347	86.5	451	3.0	5.0	105
PS–Zr12Prop	141	4.5	349	83.7	455	5.9	6.0	107
PS–Zr12AcMc	156	3.1	328	82.1	465	7.7	7.0	115
PS–Zr12Vin	136	5.9	358	84.3	455	4.6	5.1	105
PS–Zr6Norb	[a]	4.8	359	93.4	441	3.4	3.4	107
PS–Zr6IbMc	[a]	3.3	342	88.4	463	5.1	3.0	107
PS–Zr6Mc	167	1.7	345	90.8	466	4.9	2.6	105

T_g = glass transition temperature.
[a] No clear onset observed.

crosslinked polystyrene commenced at higher temperatures, and that char formation increased with increasing crosslinking density [22]. We found previously for **PS–Zr6Mc** that increasing cluster proportion and thus increased crosslinking correlated with increased char formation [12]. The fact that a crosslinked polymer, **PS–Zr12AcMc**, and a non-crosslinked polymer, **PS–Zr12Prop**, had the highest char yields among the investigated samples leads to the conclusion that crosslinking is not the decisive factor. Instead, the main influence of the clusters on the thermal properties appears to be that of a nanofiller.

The glass transition temperatures (T_g) of the hybrid polymers were 5–7 °C higher than that of pristine **PS** (Table 3). The origin of the extraordinarily high T_g of **PS–Zr12AcMc** (115 °C) is uncertain. In addition, DSC scans were performed from room temperature to 450 °C to observe events other than the glass transition. There was an endothermic event at around 350 °C in pristine **PS**, ascribed to depolymerization reactions [23], followed by a strong exothermic event due to combustion. This exothermic event was shifted to slightly higher values in the hybrid polymer samples, and the endothermic event was absent. Additional signals, caused by phase-separated cluster domains [24] or by curing of the polymers due to unreacted groups, were not observed.

4. Conclusions

Inorganic–organic hybrid polymers with zirconium oxo clusters $Zr_6O_4(OH)_4(carboxylate)_{12}$ and $Zr_{12}O_8(OH)_8(carboxylate)_{24}$ as the inorganic entities were prepared through a stepwise free radical polymerization of styrene. When clusters with methacrylate ligands were used, crosslinked materials were obtained which swelled in toluene, as expected for crosslinked polymers [6,20]. The onset temperatures of thermal decomposition and the glass transition temperatures (T_g) were shifted to higher values compared to cluster-free **PS**. For comparison, blending of non-functional POSS into vinyl ester, poly(methyl methacrylate) or polycarbonate had almost no or a slight negative influence on T_g [10].

Polymerization of styrene in the presence of **Zr6Norb** or **Zr12Vin** led to soluble polymers. This is attributed to the low propagation rates of these carboxylate ligands. The absence of gel formation during the 60 °C heating period in the **Zr12Vin** case indicated that the cluster actually acted as a polymerization inhibitor. Longer gelation times were observed and soluble polymers were also obtained when Zr_{12} clusters with acetate or propionate ligands were used as additives because crosslinking is not possible in this case. However, despite the absence of crosslinking, the hybrid polymers had higher onset temperatures of thermal decomposition and the glass transition temperatures which were comparable to the crosslinked samples.

The comparison of the thermal properties of non-crosslinked and crosslinked samples thus shows that the origin of the improvements in thermal stability is mainly due to the filler effect of the clusters rather than in their participation in network formation. Crosslinking provides extra benefits, such as rendering the hybrid polymers insoluble.

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