Macromolecules **2008,** *41,* 1131−1139

Atom Transfer Radical Polymerizations of Complexes Based on Ti and Zr Alkoxides Modified with β-Keto Ester Ligands and Transformation of the Resulting Polymers in Nanocomposites

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Received May 14, 2007; Revised Manuscript Received December 2, 2007

ABSTRACT: Well-defined complexes of Ti and Zr alkoxides and β-keto ester ligands carrying polymerizable double bonds were copolymerized with methyl methacrylate applying atom transfer radical polymerization. The structure and the morphology of the obtained hybrid polymers were investigated using NMR, FT-IR, and size exclusion chromatography. All methods revealed an incorporation of both comonomers in the polymer backbone. NMR and FT-IR analyses demonstrated that after polymerization the chemical linkage between the metal alkoxides and the organic macromolecules was preserved. The alkoxide-containing macromolecules were used as precursors in the formation of metal oxide-containing nanocomposites applying the sol−gel process. The decomposition temperature of the final nanocomposites increased depending on the chemical composition of the materials. Small-angle X-ray scattering investigations revealed a short-range order for the polymers containing Ti-alkoxides which disappeared after carrying out the sol−gel process due to the hydrolysis of the well-defined complexes. Transmission electron microscopy showed the formation of amorphous metal oxide nanoparticles inside the polymer network with diameters of a few nanometers. The particles were highly dispersed due to the low mobility of the alkoxides in the matrix during the sol−gel process.

Introduction

Recently, hybrid materials gained much attention because of their synergetic properties arising from the combination of both inorganic and organic components, mostly at the molecular level.[1−3] An important challenge in their formation is the prevention of agglomeration of the inorganic components in the polymer matrix, which can be reached by a covalent connection between the inorganic and the organic moieties limiting the diffusion of the formed inorganic particles in the organic network. Furthermore, a stable connection between the organic matrix and the metal alkoxide precursor hinders microphase separation, which is frequently observed when particles and clays are used for the reinforcement of the polymer materials.[4] In the past decades the sol−gel process became one of the most important pathways in the preparation of oxidic components in hybrid inorganic−organic materials due to its mild reaction conditions and its inertness toward many organic functionalities during network formation.[5] While for the silicon-based sol−gel process the reaction parameters are well understood and tailoring of the structure and composition of the resulting materials is nowadays state of the art, the transition-metal-based sol−gel process is much more difficult to control. The major reasons for this difference are the more electropositive character of the metals, leading to a more efficient nucleophilic attack and the larger number of coordination sites usually varying between four and nine depending on the metal, resulting in a higher reactivity.[5−7] One way to reduce this reactivity is to use bidentate ligands that can block additional coordination sites. The second advantage of such ligands is the possibility to introduce organic functionality that usually survives the sol−gel conditions and can be detected in the final material.[8] Compounds used as such controlling agents are carboxylic acids,[9,10] diols,[11] β-diketones,[12] and isoeugenole-type compounds.[13] β-Keto esters with attached polymerizable bonds such as 2-(methacryloyloxy)ethyl acetoacetate (HAAEMA) have only been rarely employed in the modification of metal alkoxides.[11,14−18] In all literature-described cases free radical polymerization was used to form the polymer matrix.[19] This technique has the advantage of being applicable to a large number of monomers under a variety of reaction conditions (temperature, solvents). However, it has the disadvantage that the polymerization occurs in an uncontrolled manner, making a well-defined design of the final polymer architecture difficult. One of the few examples of applying a more controlled polymerization technique was the use of ring-opening metathesis polymerization in combination with the sol−gel process for obtaining hybrid inorganic−organic networks with low shrinkage.[20,21] However, this technique is limited to a very small selection of monomers.

The recently developed controlled radical polymerization techniques allow well-controlled designs of different polymer architectures.[22] From these methods, atom transfer radical polymerization (ATRP) is most often applied due to its good control of the molecular weight and polydispersity of the resulting polymers, the possibility to use a broad variety of different monomers, and the fact that a simple catalyst system can be used.[23] Various hybrid materials were already synthesized using this technique starting from inorganic building blocks such as inorganic clusters,[24,25] metal alkoxides,[26] and nanoparticles[27,28] which were modified with initiating groups active for ATRP. In other studies, such building blocks as methacryloyl-modified polyhedral oligomeric silsesquioxane (POSS) cages were used as monomers in ATRP.[29−31] The well-controlled manner of the polymerizations was not affected by the inclusion of all of these inorganic moieties. Enhanced mechanical and thermal properties could be obtained by using such well-defined building blocks.

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10.1021/ma0710838 CCC: \$40.75

Here we report an approach for the synthesis of inorganic−organic nanocomposites based on transition metal oxides well dispersed into an organic polymer prepared by ATRP. Ti and Zr alkoxides were modified with β-keto esters carrying the polymerizable group 2-(methacryloyloxy)ethyl acetoacetate. The well-defined coordination compounds were copolymerized with methyl methacrylate (MMA) by ATRP to produce copolymers containing metal alkoxides. The alkoxides were transferred into metal alkoxides through controlled sol−gel reaction.

Experimental Section

Materials. CuBr (Fulka, purum, p.a., ≥ 98.0%) was stirred overnight with concentrated acetic acid, washed with absolute ethanol, and dried in vacuum. Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) and ethyl α-bromoisobutyrate (Aldrich, 98%) were distilled and kept under an argon atmosphere. Methyl methacrylate (Fluka, purum, ≥99.0%) was dried over CaH_2, distilled under argon, and kept at −20 °C. 2-(Methacryloyloxy)ethyl acetoacetate (Aldrich, 95%) was distilled under argon. Titanium isopropoxides (Aldrich, 97%), titanium ethoxides (Fluka, purum), and zirconium isopropoxides (ABCR; 70−75% in heptane) were used as received. All solvents were dried with standard procedures and stored under an argon atmosphere. Operations where the absence of humidity or oxygen was required, e.g., the handling of metal alkoxides and the polymerization procedures, were carried out under argon atmosphere using the Schlenk technique.

Measurements. Solution NMR spectra were recorded on a Bruker Avance 300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) equipped with a 5 mm inverse-broadband probe head with a *z*-gradient unit. Solid-state NMR spectra were recorded on a Bruker DPX 300 (^{13}C at 75.40 MHz) equipped with a 4 mm broadband MAS probe head. ^{13}C spectra were recorded with ramped CP/MAS spectra (cross-polarization and magic angle spinning). Rotor spinning speed was usually 6−8 kHz. Relative size exclusion chromatography (SEC) measurements in tetrahydrofuran were performed 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. Molecular weight analyses were calculated using Waters Millennium software including the GPC/V option and related to an internal standard (biphenyl ether). FT-IR spectra were recorded on a Bruker Tensor 27 instrument working in ATR MicroFocusing MVP-QL with a ZnSe crystal. The software used for analysis was OPUS version 4.0. Thermogravimetric analyses (TGA) were carried out with a Shimadzu TGA-50 at heating rates of 5 °C min^{-1} under air. Differential Scanning Calorimetry (DSC) measurements were performed on a DSC823^e with liquid nitrogen cooling from Mettler Toledo. The polymer samples were powdered and filled into 40 μL aluminum crucibles. Measurements were done under N_2 atmosphere, and a typical temperature program consisted of cooling with 20 °C/min to −50 °C and a subsequent heating with 20 °C/min to 200 °C. Samples for transmission electron microscopy (TEM) measurements were prepared by ultrasonically dispersing the particles in ethanol prior to deposition on a carbon-coated TEM Cu grid. TEM measurements were performed on a JEOL JEM-200CX or a JEOL JEM-100CX (USTEM, Vienna University of Technology). Small-angle X-ray scattering was performed using a pinhole camera with a rotating anode generator (Nanostar from Bruker AXS, Karlsruhe, with Cu Kα radiation from crossed Göbel mirrors). The X-ray patterns were radially averaged to obtain the intensity in dependence on the scattering vector $q = (4\pi/\lambda) \sin \theta$, with 2θ being the scattering angle.

Synthesis of β-Keto Ester Modified Metal Alkoxides. The β-keto ester modified alkoxides were prepared following a previously described procedure in which the β-keto ester ligand (2-(methacryloyloxy)ethyl acetoacetate) was added dropwise to a solution of a metal alkoxide in an absolute solvent (*n*-heptane, dichloromethane, toluene, alcohol) in ratios between 1:1 and 4:1 under stirring.[32] The reaction was carried out overnight, and the solvent was evaporated afterwards under reduced pressure. The resulting product was either an oily liquid (Ti compounds) or a solid (Zr compounds) soluble in most organic solvents (dichloromethane, *n*-heptane, toluene).

(Co)polymerization. All polymerizations were carried out according to standard ATRP procedures described in the literature.[23] Copolymerizations were carried out in toluene or in bulk using CuBr catalyst, PMDETA ligand, and ethyl bromoisobutyrate as initiator at 85 °C (monomer:CuBr:PMDETA:initiator = 200:1:1:2). The ratios between the HAAEMA type monomers and MMA were 1:1, 1:5, and 1:10. Pure HAAEMA monomer was also copolymerized with MMA to compare the results of uncoordinated ligands with those of metal complexes. The polymerization time was between 4 and 6 h. The reactions were quenched by precipitating the reaction mixture in petroleum ether. Typical example for homopolymerization of HAAEMA: 5 mL (0.026 mol) of HAAEMA, 0.019 g (0.13×10^{-3} mol) of CuBr, and 0.039 mL (0.262×10^{-3} mol) of ethyl 2-bromoisobutyrate were added to a dry flask under an inert gas atmosphere. The flask was freeze-dried three times and filled with argon. 0.028 mL (0.13×10^{-3} mol) of PMDETA was added, and the reaction was placed in an oil bath at 85 °C. The mixture was stirred at this temperature for 6 h. The polymer was precipitated in petroleum ether, washed, and dried under vacuum. ^{1}H NMR ($CDCl_3$, 25 °C, δ/ppm): 12.01 (OH^{enol}), 5.04 ($(CO)_2CH^{enol}$), 4.30−4.15 (br, 4H, OCH_2CH_2O), 3.55 (br, 2H, $(CO)_2CH_2$), 2.3 (s, 3H, CH_3CO), 1.94 (s, 1H, CH_3C), 1.91−1.62 (br, $CH_2C(CH_3)-$). Yield (gravimetric calculated): 73%. Typical example for copolymerization of HAAEMA with MMA (1:5): 2 mL (0.011 mol) of HAAEMA, 5.55 mL (0.053 mol) of MMA, 0.030 g (0.21×10^{-3} mol) of CuBr, and 0.062 mL (0.420×10^{-3} mol) of ethyl 2-bromoisobutyrate were added to a dry flask under inert gas atmosphere. The flask was freeze-dried three times and filled with argon. 0.044 mL (0.21×10^{-3} mol) of PMDETA was added, and the reaction was placed in an oil bath at 85 °C. The mixture was stirred at this temperature for 6 h. The polymer was precipitated in petroleum ether, washed, and dried under vacuum. ^{1}H NMR ($CDCl_3$, 25 °C, δ/ppm): 12.01 (OH^{enol}), 4.99 ($(CO)_2CH^{enol}$), 4.29−4.14 (br, OCH_2CH_2O), 3.67 (CH_3C), 3.55 (br, $(CO)_2CH_2$), 2.3 (br, CH_3CO), 1.95 (s, CH_3C), 1.92−1.43 (br, $CH_2C(CH_3)-$). ^{13}C NMR ($CDCl_3$, 25 °C, δ/ppm): 202.1 (CH_3CO), 176.1 (CH_3OCO-), 168 ($OCOCH_2CO$), 167.1 (COO), 63.1 (OCH_2CH_2O), 62.1 (OCH_2CH_2O), 43.1 ($CH_2C(CH_3)-$), 42.3 ($CH_2C(CH_3)-$), 51.1 ($(CO)_2CH_2$), 25.4 (CH_3CO), 18.2 ($CH_3C(CH_2)-$). Yield (gravimetric calculated): 79%. Typical example for copolymerization of $M(OR)_3AAEMA$ (M = Ti, Zr; R = Et, ^{i}Pr) with MMA (1:5): 3.98 g (0.011 mol) of $Ti(OEt)_3AAEMA$, 5.55 mL (0.053 mol) of MMA, 0.030 g (0.21×10^{-3} mol) of CuBr, and 0.062 mL (0.420×10^{-3} mol) of ethyl 2-bromoisobutyrate were dissolved in 25 mL of solvent (toluene, dichlorobenzene) in a dry flask under inert gas atmosphere. The flask was freeze-dried three times and filled with argon. 0.044 mL (0.21×10^{-3} mol) of PMDETA was added, and the reaction was placed in an oil bath at 85 °C. The mixture was stirred at this temperature for 6 h. The polymer was precipitated in dry petroleum ether, washed, and dried under vacuum. The copolymers were insoluble in common organic solvents. ^{13}C CP MAS (25 °C, δ/ppm): 188.7 (CH_3CO), 176.1 (CH_3OCO-), 166.8 ($OCOCHCO$), 167.1 (COO), 88.2 ($(CO)_2CH$), 73.2 (CH^{OEt}), 63.1 (OCH_2CH_2O), 62.1 (OCH_2CH_2O), 42.5 ($CH_2C(CH_3)-$), 41 ($CH_2C(CH_3)-$), 25.4 (CH_3CO), 18.4 (CH_3^{OEt}), 18.2 ($CH_3C(CH_2)-$). Yield (gravimetric calculated): 81%.

Sol−Gel Process. The purified copolymers containing Ti and Zr alkoxides were precipitated in petroleum ether, dried, washed with heptane, powdered, and kept under inert atmosphere. For the sol−gel process the copolymers (~1 g of copolymer) were powdered and transferred into a desiccator under a saturated water atmosphere and kept for 7 days, either at room temperature or at 40 °C. Afterward, the polymers were dried under reduced pressure. ^{13}C CP MAS (25 °C, δ/ppm): 196 (CH_3CO), 175 (CH_3OCO-), 168 ($OCOCHCO$), 167 (COO), 87.7 ($(CO)_2CH$), 63 (OCH_2CH_2O), 62.4 (OCH_2CH_2O), 48.5 ($CH_2C(CH_3)-$), 42.6 ($CH_2C(CH_3)-$), 25.4

Scheme 1. Schematic Representation of the Two Possible Pathways for Obtaining Metal Coordinating Polymers by Atom Transfer Radical Polymerization (ATRP)[a]

[a] M = metal complex, $M(OR)_4$ = metal alkoxide (M = Ti, Zr, R = ^{i}Pr, Et).

Table 1. Size Exclusion Chromatography (SEC) Data for the 2-(Methacryloyloxy)ethyl Acetoacetate−Methyl Methacrylate Homo- and Copolymers Obtained without Metal Alkoxides[a]

polymer	ratio between monomers	M_n	PDI	DP_n theor	DP_n obsd from SEC	yield (%)
poly(HAAEMA)		37 036	1.23	200	175	68
PMMA		20 395	1.18	200	203	83
poly(HAAEMAcoMMA)	1:1	28 117	1.39	100	90	74
poly(HAAEMAcoMMA)	1:1	45 261	1.70	200	144	63
poly(HAAEMAcoMMA)	1:5	27 915	1.82	200	195	71
poly(HAAEMAcoMMA)	1:10	30 572	1.58	200	275	76
poly(HAAEMAcoMMA)	1:10	43 249	1.89	400	360	69

[a] M_n = numeric molecular mass, PDI = polydispersity index (M_n/M_w), and DP_n = degree of polymerization.

(CH_3CO), 18.2 ($CH_3C(CH_2)$−). Yield (gravimetric calculated): 81%.

Results and Discussion

Synthesis of HAAEMA−MMA Copolymers. Well-defined metal oxide nanoparticles were prepared in a polymer matrix previously synthesized by ATRP. For this purpose model HAAEMA−MMA copolymers were synthesized by ATRP in a first step. The optimized process was then applied to the synthesis of $M(OR)_3$AAEMA−MMA copolymers (M = Ti, Zr and R = Et, ^{i}Pr). The obtained hybrid copolymers where exposed to water vapor to carry out the sol−gel process for the hydrolysis of the metal alkoxides and, thus, the formation of small metal oxide nanoparticles inside the polymer matrices.

Several studies reported the synthesis and characterization of Ti and Zr alkoxides with β-diketones and β-keto esters.[12,17,18] We previously described the synthesis and characterization of well-defined coordination compounds of Ti and Zr alkoxides with acetoacetaoxy alkyl methacrylate ligands.[32] In these studies we were able to prepare the binuclear coordination monomers $[Ti(OEt)_3AAEMA]_2$, $[Ti(O^iPr)_3AAEMA]_2$, and $[Zr(O^iPr)_3AAEMA]_2$. All these compounds do not show metal alkoxide-catalyzed transesterification reactions, which is a side reaction that is sometimes observed with this type of compounds and would lead to partial decomposition of the monomers, and thus well-defined polymers can be expected by applying ATRP. Recently, poly(HAAEMA) homopolymers were prepared by reversible addition−fragmentation chain transfer (RAFT) radical polymerization[33] and were found to self-assemble into a hierarchical superstructure of double-stranded helical tubes with either screw sense.[34] To the best of our knowledge, no reports on the use of ATRP for metal alkoxide−HAAEMA monomers were given yet.

Compared to other coordinating polymers, such as amine containing systems, no coordination of the copper catalyst to the polymer by partial or full ligand exchange should occur in these systems. The reasons for this behavior lies in the higher stability of the tridentate PMDETA/copper complex compared to β-keto ester complexes. In addition in the cases of the polymerizations of the metal alkoxide-containing monomers, the titanium and zirconium atoms are much more oxophilic than copper. We carried out UV studies to experimentally support this theoretical prediction. These studies showed no coordination of the Cu−PMDETA complex to the HAAEMA monomer from room temperature up to the polymerization temperature of 85 °C. In this temperature range no change in the absorption band of the copper complex was detectable. Additional FT-IR investigations showed that the HAAEMA ligand was maintaining its keto form without any signs of coordination in the presence of the Cu complex.

Possible pathways for the preparation of hybrid inorganic−organic polymers containing metal alkoxides are presented in Scheme 1; either a ligand containing a polymerizable group is coordinated to a metal alkoxide (M) and this compound is used in a polymerization reaction or a polymer containing the coordination ligands is formed in a first step and the coordination of the metal alkoxides occurs subsequently. The latter pathway has the disadvantage that control over the coordination of the metal alkoxides is not easy to obtain and that cross-linked systems result immediately after mixing the ligand containing polymer and the metal alkoxides. Furthermore, because of the diffusion limits in such a pre-cross-linked system, it is unlikely that all of the metal alkoxides can reach the coordination sites. Therefore, we focused on the first pathway, the latter one being still investigated.

We prepared model compounds based on uncoordinated HAAEMA−MMA (co)polymers in ratios of 1:1, 1:5, and 1:10 between the two comonomers. Polymerizations were performed under previously optimized conditions. The ^{1}H NMR analyses showed the presence of the methyl protons of the polymer backbone between 0.8 and 1.2 ppm, while the specific signals of acetoacetoxy units were present at 2.28 ppm (CH_3CO) and 3.55 ppm ($COCH_2CO$). These data are consistent with previously reported data for poly(HAAEMAcoMMA)[35] and polyHAAEMA.[34]

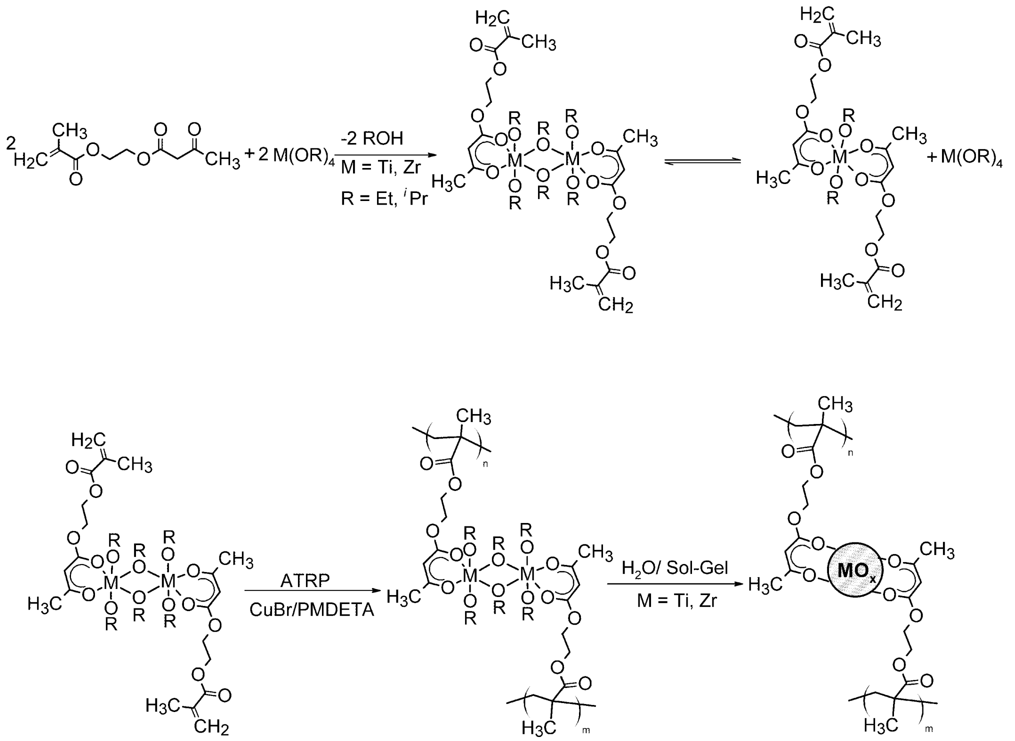
SEC results revealed that the molecular weight distribution was monomodal, and the calculated and experimentally found molecular weights are in good agreement (Table 1). ^{1}H NMR analysis showed that both monomers were incorporated into the polymer backbone. Polydispersities of the resulting polymers were between 1.2 and 1.89, which is rather high for a controlled polymerization. Broad polydispersities were also observed by Krasia et al., who investigated the ATRP of HAAEMA.[33] In our example the broad polydisperisty could be due to the different reactivity of the two monomers or due to a kind of self-organization of the copolymers. Different side groups of HAAEMA and MMA can induce different propagation rates and different reactivity of the dormant carbon−halogen terminals, which may broaden the molecular weight distribution. Such

Table 2. Thermogravimetric Analyses Results of Copolymers Obtained from Monomers Containing Ti and Zr Alkoxides as Well as Their Homologues after Carrying out the Sol−Gel Process[a]

copolymer	ratio between monomers	T_{d1}, °C	T_{d2}, °C	mass loss (1), %	mass loss (2), %	residual mass, %
poly(HAAEMAcoMMA)	1:5		280		100	0
poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA]	1:5	84	290	14.6	72.7	12.7
TiO$_2$-Poly(AAEMAcoMMA)	1:5		290		87.3	12.7
poly(HAAEMAcoMMA)	1:10		251		100	0
poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA]	1:10	87	266	13.8	81.2	5.1
TiO$_2$-Poly(AAEMAcoMMA)	1:10		273		93.1	6.9
poly[Zr(O^{i}Pr)$_3$AAEMAcoMMA]	1:5		271	6.27	78.2	14.3
ZrO$_2$-Poly(AAEMAcoMMA)	1:5		270		83.9	16.1
poly[Zr(O^{i}Pr)$_3$AAEMAcoMMA]	1:10	52	251	10.4	78.3	11.3
ZrO$_2$-Poly(AAEMAcoMMA)	1:10	130	269	8	81	11

[a] T_{d1} = first onset temperature, T_{d2} = second onset temperature, MMA = methyl methacrylate, and HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate.

Scheme 2. Coordination of Ti and Zr Alkoxides with 2-(Methacryloyloxy)ethyl Acetoacetate, Copolymerization with Methyl Methacrylate, and the Sol−Gel Process[a]



[a] ATRP = atom transfer radical polymerization, PMDETA= pentamethyldiethylenetriamine.

a broadening phenomenon during the random copolymerization has also been observed in the case of copolymerization of 3-(methoxysilyl)propyl methacrylate with MMA.[36] As mentioned before, a coordination of the catalyst to the pendant acetylacetoxy groups can be ruled out to be responsible for the quite high polydispersities.

TG analyses of the copolymers in 1:5 and 1:10 ratios between HAAEMA and MMA revealed that the copolymers show an onset temperature of decomposition at 280 °C for the 1:5 ratio compared to 251 °C for the 1:10 ratio (Table 2), which displays a decrease of the thermal stability with the increase of the MMA content. The total mass change is more than 99%, proving that the polymer is completely decomposed at 650 °C. The glass transition temperatures T_g measured from differential scanning calorimetry (DSC) of the copolymers were between 91 and 130 °C increasing with the increase of the MMA content.

Synthesis of Metal Alkoxide-Containing Polymers. Previous studies of the metal alkoxide−HAAEMA complexes showed that the coordination compounds between Ti alkoxides and β-keto esters in a 1:1 ratio appear as alkoxide-bridged dimers in solid state with chelating ethyl acetoacetate ligands, presenting a centrosymmetric structure.[32] In solution, because of ligand exchange reactions, there is an equilibrium between the dimeric species and the monomeric disubstituted species including some free metal alkoxides (Scheme 2). Complete avoidance of cross-linking between single polymer chains is not possible on the basis of this equilibrium, and therefore polymerization reaction should still result in at least partially cross-linked polymers. First attempts to use coordinated Ti alkoxides with HAAEMA type ligands as monomers in ATRP were reported by us recently.[35]

Polymerizations of the coordinated compounds were carried out under the same optimized conditions used for the non-metal-containing copolymers. CuBr/PMDETA was applied as a catalyst, 2-ethylbromoisobutyrate as initiator, and toluene as solvent. The temperature of the polymerization reactions was maintained at 85 °C, and the reaction time was 6 h.

When homopolymerization of the metal complexes was applied, gelation occurred in minutes after the start of the polymerization. The reason for this behavior is ligand exchange

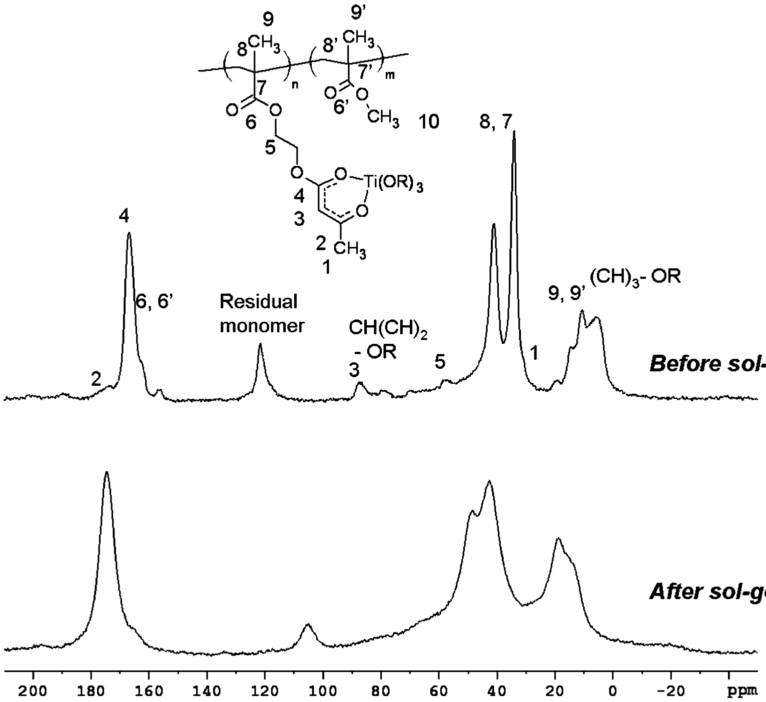


Figure 1. ^{13}C MAS NMR spectra of poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA] (up) (synthesized at 85 °C, monomer:CuBr:PMDETA:initiator = 200:1:1:2 equivalents, ratio between 2-(methacryloyloxy)ethyl acetatoacetate and methyl methacrylate 1:5) and spectra of poly(TiO$_2$−AAEMAcoMMA) (obtained by the sol−gel process at room temperature in an water saturated atmosphere from the corresponding copolymer) and the respective assignments.

and the resulting equilibrium already shown in Scheme 2. The bifunctional complexes in this equilibrium act as cross-linkers between single polymer chains.[35] Hence, the metal complexes were used in copolymerization reactions with methyl methacrylate to decrease the number of pending metal alkoxides attached to each polymer chain and thus the probability of cross-linking. However, even with a decreased amount of metal complexes in the polymer chain, cross-linking could not be completely avoided. As a consequence, ratios between metal containing monomers and MMA of 1:5 and 1:10 were chosen to increase the gelation time and, hence, to obtain a better control over the polymerizations. As a difference to their non-metal-containing homologues, Ti and Zr alkoxide containing polymers could not be analyzed via SEC due to the insolubility of the cross-linked systems in common organic solvents.

The metal-containing copolymers were analyzed by FT-IR and solid-state NMR spectroscopy. A ^{13}C CP/MAS spectrum of poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA] in a 1:5 ratio between the two comonomers is shown in Figure 1. The resonances of the CH_3 groups of the isopropoxy unit are found at 10.0 ppm while the CH_3 of the AAEMA ligand are located at 18.0 ppm (methacrylate part) and at 20.0 ppm (keto-ester part). Evidence for the polymerization of the AAEMA ligand is obtained by the signal at 41.0 ppm, corresponding to the quaternary carbon atoms of the polymer chains. Glycol C atoms are observed at 57.1 ppm, and the methylene carbons (*CH*) of the isopropoxy groups result in a signal at 79.1 ppm.

The chelating form present in the final polymer is proven by the *CH* group of the coordinated ligand at 87.7 ppm which clearly revealed that coordination is still maintained after polymerization. In the copolymerization of metal-free HAAEMA no free monomers could be detected after polymerization at 85 °C for 6 h. We used these optimized conditions also for the monomers coordinated on the metal alkoxides. However, because of cross-linking, the hybrid materials still show a signal at 121.6 ppm which can be assigned to residual olefinic carbons of the monomers.[19] Hence, a full conversion of the double bonds was not achieved during the 6 h of the polymerization. The carbonyl region shows resonances for the chelating form at 166.8 and 189.7 ppm. There are no signals corresponding to uncoordinated ligands, which proves that coordination is maintained during the polymerization process. It was important for further sol−gel reactions applying the obtained polymers that the alkoxides were still bound to the metal centers and that a good linkage between the inorganic and organic phase is achieved.

The FT-IR data of the samples with the metal alkoxides also proved that the linkage between the inorganic and the organic part still exists after the polymerization. The typical bands at 1626/1611 and 1527 cm^{-1}, (C═C) and (C−O) stretching of the chelating form of the ligand, are still present. The shifts are characteristic for coordinated diketones and keto esters.[37] Also, these data are sustained by the already reported ones in the cases of HAAEMA ATRP systems.[32]

Sol−Gel Processing of the Polymers Containing the Metal Alkoxides. The sol−gel process was carried out using the metal alkoxide containing polymers as powdered samples in a desiccator under a saturated water atmosphere. The copolymers were kept inside for 7 days, either at room temperature or at 40 °C. Afterwards, the polymers were dried under reduced pressure.

After the sol−gel reaction a general broadening of the ^{13}C NMR peaks in the solid-state spectra was observed without changes of the peak positions of the carbons of the polymer chains (42.6 and 48.5 ppm). No signal for the *CH* carbon of the isopropoxy moieties at 79 ppm was detected, and the signal of the CH_3 groups of the isopropoxy rests around 13 ppm was only observed as a small shoulder. The *CH* groups of the coordinated ligand formally present at 87.7 ppm were also not visible anymore. However, the carbonyl region presents almost the same shifts as before (165, 174.5, and 197 ppm). It is difficult to make a statement whether the AAEMA ligand is still coordinated. Most likely parts of the ligand were hydrolyzed during the sol−gel reaction. Hoebbel et al. investigated the hydrolysis behavior of different complexes of β-keto esters

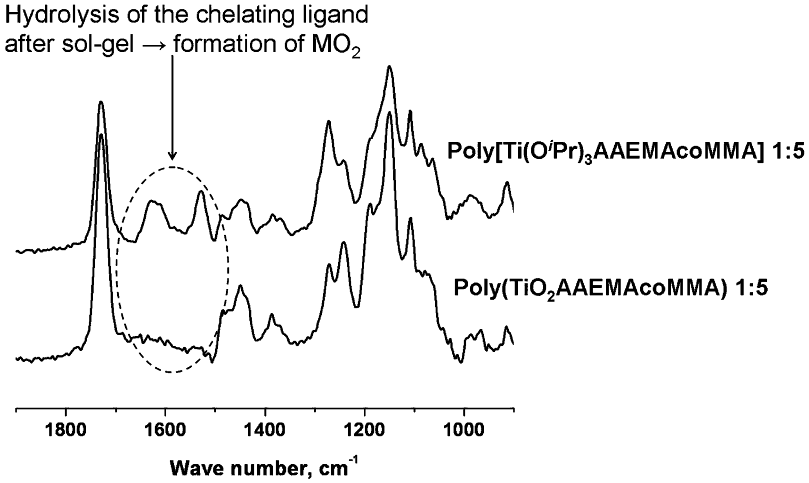


Figure 2. FT-IR of the poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA] (up) (synthesized at 85 °C, monomer:CuBr:PMDETA:initiator = 200:1:1:2 equivalents, ratio between 2-(methacryloyloxy)ethyl acetatoacetate and methyl methacrylate 1:5) and spectra of poly(TiO$_2$−AAEMAcoMMA) (obtained by the sol−gel process at room temperature in a water-saturated atmosphere from the corresponding copolymer) and the respective assignments.

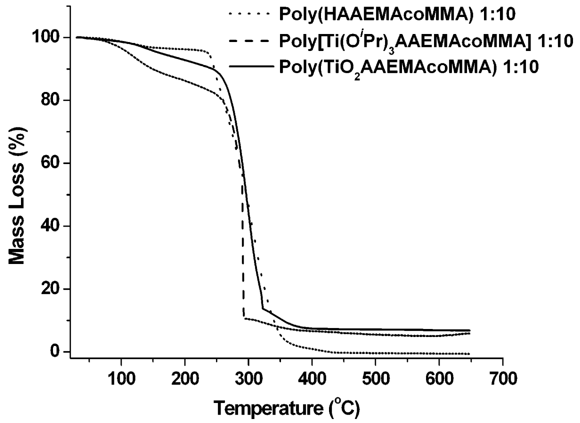


Figure 3. Thermogravimetric analysis of poly(AEEMAcoMMA) 1:10; poly[Ti(O^{i}Pr)$_3$AAEMAcoMMA] 1:10; and poly(TiO$_2$−AAEMAcoMMA) (after sol−gel) (HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate, MMA = methyl methacrylate).

ligands and Ti or Zr alkoxides[18] and showed that even at small water-to-metal ratios some of the methacryloyloxyethyl acetoacetate ligands were hydrolyzed.

FT-IR data after applying the sol−gel process revealed the disappearance of the characteristic bands of the coordinated ligands at 1626/1611 and 1527 cm^{-1} (Figure 2) and the appearance of a broad band between 1650 and 1700 cm^{-1}. These facts suggest that some of the chelating ligands are hydrolyzed, and the keto form of the ligands is present instead of the chelating one. These results are consistent with the NMR results.

Thermogravimetric Analyses of the Polymers. TG analyses for both 1:5 and 1:10 copolymers with and without metal alkoxides were carried out. As mentioned before, the analyses of the copolymers in 1:10 ratios reveal that the copolymers without metal alkoxides (HAAEMA:MMA 1:10) show an onset temperature of decomposition at 251 °C (Table 2). The total mass change is more than 99%, proving that the polymer completely decomposes at 650 °C. Contrarily, the metal-containing copolymers showed two onset temperatures (Figure 3). The first one is located around 85 °C, which is due to the cleavage of alkoxide ligands and the decomposition of the Ti− and Zr−β-keto ester complexes.[38] The mass loss for this first event which takes place before 200 °C is around 13%. The second onset temperature for decomposition was detected at 266 °C for Ti isopropoxides and at 260 °C for Ti ethoxides, which is most likely due to the decomposition of the polymer main chain. We observed also a slight increase in the onset temperature in the cases of the copolymers containing metal alkoxides compared with the ones without metals, which is most likely due to cross-linking which blocks depolymerization mechanisms. However, these results are not very accurate because the onset temperatures used for this comparison are strongly influenced by the slopes of the tangents before and after the event. The mass loss due to the more volatile alkoxides falsifies the real value of the degradation of the main polymer chain. The residual mass at 650 °C is 5.1% for polymers containing Ti isopropoxides. The mass of the residues can be attributed to the formation of TiO$_2$. This seems very realistic after the analyses of the copolymers with 1:5 ratio between HAAEMA [or Ti(OR)$_3$AAEMA] and MMA. In this case the final residual is higher (around 13%) corresponding to the higher quantity of metal oxide in the copolymer. The residual mass is similar to the calculated metal content. However, without clear information about the molecular mass a strict calculation cannot be made. This is in accordance with the data reported by Chang et al. for the PMMA−M(OBu)$_2$EAA$_2$ nanocomposites (M = Ti, Zr).[38] However, an increase of the thermal stability is expected when transferring the alkoxides in a sol−gel network. Comparing the copolymers without metals in 1:5 and 1:10 ratio between HAAEMA and MMA, it is clear that the onset temperature corresponding to the degradation of the main polymer chains is decreasing with the increasing of the MMA content, so the thermal stability is lower for higher MMA content. However, decreasing the MMA content the gelation is faster and the polymerization less controlled; therefore, an optimum has to be found between a good thermal stability and a convenient MMA content. The copolymers containing isopropoxy groups show an increase in the thermal stability compared to the copolymers without metals.

The results summarized in Table 2 prove that the metal alkoxide monomers are incorporated into the copolymer chains. The obtained structure of the metal-containing polymers is consistent with the one predicted and allows further reaction via the sol−gel process.

After carrying out the sol−gel process, the excess of volatiles and water was removed in vacuum. The thus-dried hybrid materials containing the amorphous metal oxide phases were analyzed by TGA (Table 2, Figure 3).

It is obvious for all samples (Ti- and Zr-modified alkoxides) that the first decomposition stage (before 200 °C) almost

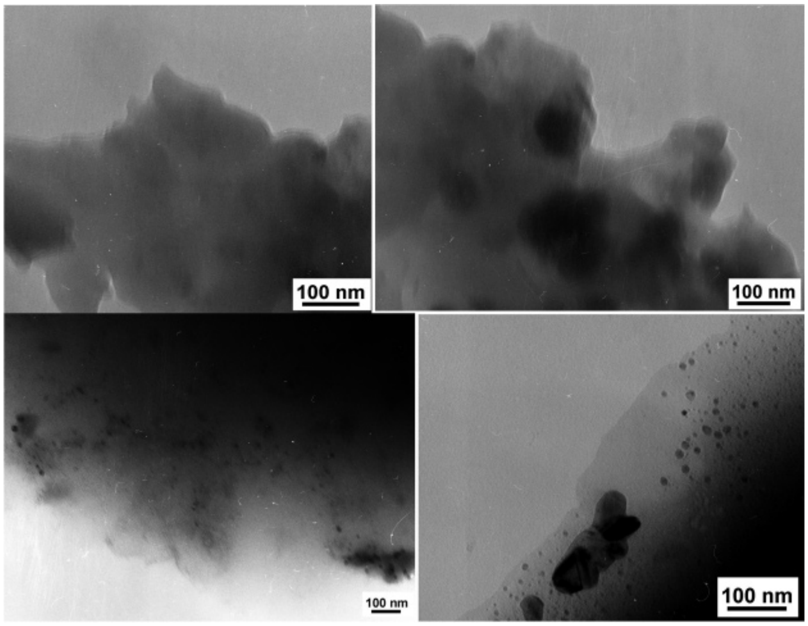


Figure 4. Transmission electron micrographs of the poly[Ti(OR)$_3$AAEMAcoMMA] (top, 1:10 and 1:5) and TiO$_2$−polyAAEMAcoMMA (bottom, 1:10 and 1:5) (HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate, MMA = methyl methacrylate).

disappeared, the mass loss in this region being below 2%. These volatiles are most likely residues of alkoxide groups and water. The second stage (decomposition of the polymer main chain) shows an increase in the decomposition temperature of the material (273 °C for the 1:10 ratio, TiO$_2$ sample). The final residual percentage is exactly the same for both the alkoxide-containing samples and the sol−gel samples.

Structure and Morphology of the Polymers. The polymers containing metal alkoxides as well as the materials obtained after carrying out the sol−gel process were analyzed by transmission electron microscopy (TEM). The resulting micrographs of the Ti alkoxide-containing polymers show a uniform distribution of the inorganic phase in the polymer matrix (Figure 4). Agglomerates or particles cannot be detected. The darker regions presented in the samples are due to variations in the thickness of the sample and not to a different material.

The morphology of the hybrid material changes drastically after the sol−gel process was applied (Figure 4, bottom). Small particles uniformly distributed in the polymer matrix are observed. The different contrast suggests that the particles are formed from compounds of a heavier element, in this case titanium. It is important to remark that all sample regions analyzed were similar, for both of the TiAAEMA complex: MMA ratios used. The diameter of the particles was ranging from a few nanometers up to 15 nm. The growing of the particles is due to a cumulative effect resulting from the partial hydrolysis of the complexes and from the presence of free titanium alkoxides, as described in Scheme 2. As determined from spectroscopic analyses, a considerable amount of the acetyl acetone ligand is hydrolyzed, leading to some extent of agglomeration.

The same trend was also observed in the cases of copolymers containing Zr alkoxides and ZrO$_2$. No agglomerates or particles could be detected in the copolymers containing Zr isopropoxides. After the sol−gel process small nanoparticles could be detected in all of the analyzed samples (Figure 5). These were most likely the result of the hydrolysis and condensation of the zirconium alkoxides and the formation of the respective oxides. The diameter of the particles was also ranging from a few nanometers up to around 20 nm.

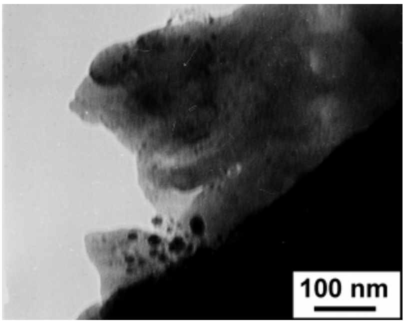


Figure 5. Transmission electron micrographs of the ZrO$_2$−polyAAEMA-coMMA (1:5) (HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate, MMA = methyl methacrylate).

SAXS. SAXS measurements were carried out for the three systems investigated: the simple copolymers, the copolymers containing metal alkoxides (Ti and Zr isopropoxides), and the copolymers with metal oxides (after sol−gel).

The copolymer without any metal alkoxides showed just a q^{-4} scattering from large units within the polymer and a broad and weak peak between $q = 8$ and $q = 12$ nm^{-1}. The polymers containing Ti alkoxides (Figure 6), before the sol−gel process, exhibit a strong order (peak at $q = 10.1$ nm^{-1}), corresponding to a repeating distance of 0.62 nm in real space. This strong order is probably due to a regular alignment of the Ti alkoxide clusters in a one-dimensional chain. The weak and broad peak at $q = 4.3$ nm^{-1} (1.5 nm in real space) is only visible in the polymer containing a higher amount of metal alkoxides and is attributed to a short-range order of the chains, i.e., a typical chain-to-chain distance.

This order is not visible any more after the sol−gel process, and only a broad peak around $q = 10$ nm^{-1} remains, which could be due to either a short-range order of the particles or the original copolymer. It is suggested that this dissolution can be attributed to the hydrolysis of the well-defined coordination compounds and the probable formation of metal oxides, which do not exhibit a well-defined order.

The interpretation of the zirconium series (Figure 7) differs in some respect. In the materials before gelation, there is a weak

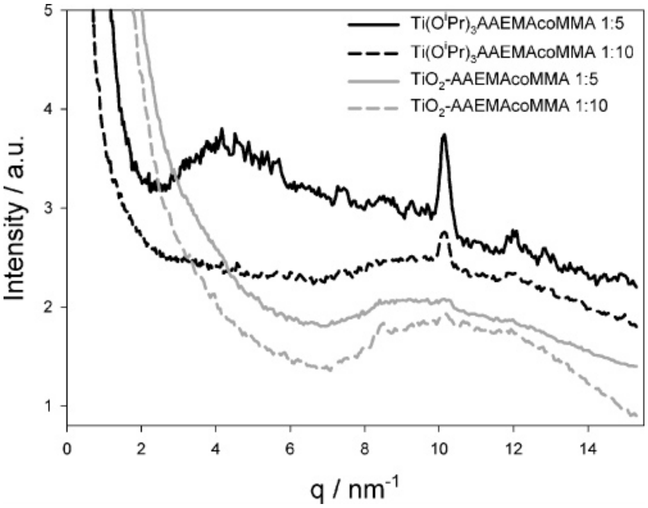


Figure 6. Small-angle X-ray scattering intensities of the copolymers containing Ti alkoxides and TiO_2 particles in 1:5 and 1:10 ratios between the two monomers. The curves are vertically shifted for better visibility (HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate, MMA = methyl methacrylate).

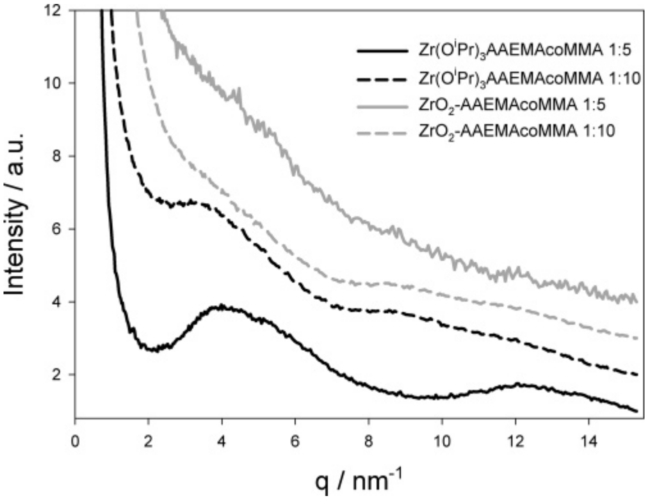


Figure 7. Small-angle X-ray scattering intensities of the copolymers containing Zr alkoxides and ZrO_2 particles in 1:5 and 1:10 ratios between the two monomers. The curves are vertically shifted for better visibility (HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate, MMA = methyl methacrylate).

short range order in the range of 1.6 nm (peak at $q = 4.0$ nm^{-1}), which is more pronounced for the material with a higher amount of zirconia. This weak order is similar to the polymer with the higher amount of Ti alkoxides, but for Zr visible in both concentrations. It is also nearly completely dissolved after the gelation process in coincidence with the results for the Ti-containing material. Only a shoulder in the scattering intensity remains, which shows just a random distribution of particles.

Differently, the scattering intensity toward very low q values follows, for the Zr samples with a 1:10 ratio between the alkoxides and the MMA series, a power law decrease with q^{-3} instead of q^{-4} as for all other samples, which could be a possible indication for the dissolution of the Zr particles or some extensive clustering.

The absence of sharp ordering of the Zr alkoxides copolymers like in the cases of the Ti alkoxide copolymers before the sol−gel reaction can be also supported by the difference in the coordination behavior of the two metals. Contrary to the preferentially six-coordinated Ti, Zr as its larger homologue offers an expandable coordination sphere with potential coordination numbers between 6 and 9. This can restrict the formation of well-defined clusters with an restricted order, leading rather to multiple species. This can explain the absence of an intense ordering in the samples containing the Zr alkoxides.

Conclusions

The well-defined coordination compounds $[Ti(O^iPr)_3AAEMA]_2$, $[Ti(OEt)_3AAEMA]_2$, and $[Zr(O^iPr)_3AAEMA]_2$ were used in ATRP copolymerization reactions with MMA in different ratios. NMR analyses revealed that the metal complexes as well as the MMA are incorporated into the polymer chain. Polydispersity indexes were rather broad between 1.23 and 1.89, which is mostly likely due to the difference in the reactivities of the two monomers resulting in a less controlled polymerization. The ^{13}C CP MAS and FT-IR analyses revealed that the coordination is still maintained after the polymerization. A slight improve in the thermal stability for the final materials was detected in the cases of the copolymers containing Ti isopropoxides by TGA analyses. The metal atoms are evenly distributed in the polymer after polymerization as shown by TEM measurements. The thus prepared metal alkoxides containing polymers were used as precursors in an aqueous sol−gel process. Solid-state NMR analyses of the resulting hybrid materials showed the disappearance of the alkoxide moieties. Formation of nanosize particles with diameters between 3 and 20 nm was proven by TEM. SAXS measurements revealed a short-range order of the polymers containing the metal alkoxides which was disturbed after the sol−gel process.

Acknowledgment. Financial support of this work by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF, Project nr.: P17424) is gratefully acknowledged.

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MA0710838