Polymer Composites Based on Reactive Carboxylate-Alumoxanes

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Summary: The possibility of applying basic aluminum carboxylates as the cross-linking monomers in radical polymerization processes as well as the initiators for ATRP of styrene and coordination ROP of heterocyclic monomers was examined. It was established, that aluminum carboxylates containing in their structure the acrylic and lauric acids derivatives show high activity in the copolymerization with vinyl monomers which results in the hybrid polymer networks formation. In the typical ATRP conditions, polymers grafted with styrene are obtained while basic aluminum 2-bromopropionate is used as the initiator. Hybrid composites i.e. core-shell nanospheres can be obtained in this way at low degree of polymerization. Nanoparticles of basic aluminum caroboxylates when reacted with triethylaluminum show high activity as initiators in the polymerization processes of ε-caprolactone, trimethylene carbonate as well as propylene and ethylene oxides. Cross-linked products in the form of a gel were formed as the result of ROP in such systems. However, linear polymers characterized by M_n above 10^4 and PDI $\geq$ 1.9 were obtained after aluminum residuals removal.

Keywords: ATRP; basic aluminum carboxylate; composites; radical polymerization; ring-opening polymerization

Introduction

Hybrid inorganic-organic polymers have become the object of intensive academic and industrial studies with respect to their potential applications as nanofillers in polymeric composites. Most of the recent studies have been focused on materials containing delaminated smectic clays or spherical nanosized silica particles modified by organic compatibilizers. The most typical modification procedures include the exchange process of inorganic cations located between negatively charged layers against hydrophobic organic onium cations, sol-gel hydrolytic condensation or reactions of OH groups located on the particle's surface with silane coupling agents. Several attempts were also made to obtain alumina nanoparticles decorated with organic ligands.[1–7] In the early 1990's Barron and coworkers reported that boehmite (γ-aluminum oxohydroxide) reacts with carboxylic acids to generate particles consisting of small boehmite core covered with carboxylate groups.

However, more detailed studies carried out in our laboratory[8] showed that the new phase is being made of basic aluminum dicarboxylates (Eq. 1).

$$[\mathrm{Al(OH)O}]_m + 2n\,\mathrm{RCO_2H} \rightarrow [\mathrm{Al(OH)O}]_{m\text{-}n}[\mathrm{AlOH(O_2CR)_2}]_n + n\,\mathrm{H_2O} \qquad (1)$$

These materials, named ''carboxylate-alumoxanes'', may be prepared with a variety of functional groups allowing the alteration of both the morphology of the formed particles and chemical properties of their surface. There are several examples of

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their interesting practical applications as nanometer-size fillers in polymer composites,[9–11] supports for olefin polymerization catalysts[12] and processable precursors to various types of alumina based ceramics.[13]

In this work we present initial results of our studies on the synthesis of composites in the course of the radical copolymerization of carboxylate-alumoxanes and their grafting with polymers. The copolymerizations were carried out in the presence of a multifunctional monomer (**I**) obtained in the reaction of boehmite with a mixture of acrylic and lauric acids.

$$[Al(OH)O]_m[AlOH(O_2CCH=CH_2)_2]_n[AlOH(O_2CC_{11}H_{23})_2]_z$$

I

For grafting reactions we used two types of aluminum hybrid compounds, one of which was a product of the reaction between boehmite and 2-bromopropionic acid (**II**) that acted as a component of the ATRP polymerization initiator.

$$[Al(OH)O]_m\{AlOH[O_2CCH(Br)CH_3]_2\}_n$$

II

The second one was a carboxylate-alumoxane containing reactive Al–O–Al bonds (**III**) that effectively initiated the coordinative polymerization of selected heterocyclic monomers. This compound was synthesized in the course of the reaction of dihydroxyaluminum laurate with triethylaluminum.

$$\{C_{11}H_{23}CO_2Al[OAl(C_2H_5)_2]_2\}_n$$

III

Experimental Part

Materials

Boehmite (Catapal®D Alumina, ca. 75 wt% Al_2O_3, CONDEA Vista), ethylene oxide (EO) (>99%, Fluka), oleic acid (≥99%, Aldrich), lauric acid (≥98%, SAFC), 2 -bromopropionic acid (pure, POCh), trifluoroacetic acid (99%, Aldrich), CuCl ≥ (99.99% Aldrich), 2,2′- bipyridyl (bpy) (>99%, Sigma-Aldrich), ethylmethylketone peroxide (MEKPO) (36 wt% solution in dimethyl phthalate, Metox-50, Oxytop) and cobalt(II) 2-ethylhexanoate (CoEH) (2% Co^{II}, 12 wt% solution in styrene/petrol spraying, ILT) were used as received without further purification. Acrylic acid (99%, Aldrich) was distilled under reduced pressure directly before use. Propylene oxide (Merck) was dried with CaH_2 and fractionally distilled on dried 5A molecular sieves. ε-Caprolactone (≥99%, Aldrich) was dried with CaH2 and distilled under reduced pressure on dried 5Å molecular sieves. Styrene (St) (≥99%, Aldrich) was dried with CaH_2, distilled under reduced pressure and stored in a refrigerator. Vinyl acetate (90 + %, Merck) was distilled under reduced pressure directly before use. Trimethylene carbonate was synthesized according to the procedure previously described.[14] Toluene (p.a., POCh) and tetrahydrofuran (p.a., POCh) were distilled from sodium/potassium alloy and benzophenone after color change to navy blue and then stored over dried 4Å molecular sieves under nitrogen. Hexane (pure, POCh), diethyl ether (pure p.a., POCh), acetone (pure, POCh), cyclohexane (pure, POCh) and xylene (mixture of isomers, pure, POCh) were used as received. Organometallic compounds: triethylaluminum (1.9M solution in toluene, Aldrich) and ethylaluminum dichloride (1.8M solution in toluene, Aldrich) were used directly from Sure/Seal™ bottles.

Material Characterization Methods

Powder X-ray diffraction data were collected on a Seifert HZG-4 automated diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The data were collected in the Bragg-Brentano ($\theta/2\theta$) horizontal geometry (flat reflection mode) between 4 and 70° (2θ) in 0.04° steps, at 20 s step^{-1}. The optics of the HZG-4 diffractometer consists of a system of primary Soller slits between the X-ray tube and the fixed aperture slit of 2.0 mm. One scattered-radiation slit of 2 mm was placed after the sample, followed by the detector slit of 0.2 mm.

Infrared spectra were collected on a Biorad 165 FT-IR spectrometer with the samples in KBr pellets or on a Nicolet 6700 FT-IR spectrometer equipped with Smart Orbit ATR accessory (Thermo Scientific).

The ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer at 400.10 MHz in $CDCl_3$ as solvent at room temperature.

The particle size distributions in the studied dispersions were determined by Dynamic Light Scattering method and a Zetasizer Nano-ZS apparatus (Malvern Instruments Ltd.) was used.

The morphology of the powdered samples was investigated by means of scanning electron microscopy (SEM). The images were recorded on a LEO 1530 microscope.

The hydrogen and carbon contents were determined with a PerkinElmer CHNS/O II 2400 instrument (PerkinElmer, Inc., Waltham, MA). The aluminum content was determined as follows. The sample was mineralized to conduct all aluminum atoms into the water- soluble form of Al^{3+}, the ions were then complexed with EDTA, and the excess of EDTA was titrated with $FeCl_3$ solution.

Relative molecular weight and polydispersity were measured by gel permeation chromatography (GPC). The GPC chromatograph was equipped with Jordi gel DVB Mixed Bed column, Lab Alliance isocratic pump (1 ml/min) and SFD refractive index detector RI-2000F. The measurements were carried out at 35 °C and chloroform was used as a solvent. The column was calibrated with narrow molar distribution polystyrene standards.

Synthesis of Carboxylate-Alumoxane (I)

Carboxylate-alumoxane **I** was synthesized in the reaction of boehmite (3.0 g, 50 mmol) with a mixture of acrylic (1.8 g, 25 mmol) and lauric (5.0 g, 25 mmol) acids, in the presence of 4-methoxyphenol (0.02 g) as a polymerization inhibitor. The mixture was refluxed in xylene (50 ml) for 3 h and centrifuged after cooling to ambient temperature, which resulted in the formation of a solid raw product, insoluble in xylene. Then all organic impurities were washed out by diethyl ether and hexane and a white powder (**I**) was obtained after drying. It contained 29.2 wt% of carbon. After the extraction step, the contents of free acids in liquid fraction (Et_2O/hexane) were determined and it was found that the conversion of acrylic and lauric acids in the reaction with boehmite was 100% and ca. 25%, respectively.

Synthesis of Carboxylate-Alumoxane (II)

Carboxylate-alumoxane **II** was synthesized according to the following procedure: boehmite (5.0 g, 83 mmol) was dispersed in 90 ml of xylene and then 2-bromopropionic acid (15 ml, 167 mmol) was added. The mixture was refluxed for 24 h, cooled to ambient temperature and centrifuged. The insoluble, raw product was purified by extraction with Et_2O and dried under vacuum. Elemental analysis: C (18.6 wt%), H (3.6 wt%) and Br (41.1 wt%).

Synthesis of Carboxylate-Alumoxane (III)

Carboxylate-alumoxane **III** was synthesized in a two-step process. First, lauric acid (7.6 g, 38 mmol) was dissolved in dried toluene (70 ml) and added dropwise to triethylaluminum solution (20 ml, 38 mmol) at –30 °C under dry nitrogen atmosphere. The reaction mixture was allowed to warm up to room temperature and stirred until liberation of gas ended.

Next, a solution of water (3.5 g, 194 mmol) in tetrahydrofuran (20 ml) was slowly added and stirred for 5 h. All volatiles were removed under vacuum, which resulted in the formation of a white solid product. The content of carbon, hydrogen and aluminum in this product was 52.2 wt%, 9.1 wt% and 12.4 wt%, respectively.

In the second step, previously synthesized compound (0.26 g, 10 mmol) was dispersed in dried toluene (10 ml) and then triethylaluminum (10.5 ml, 20 mmol) was added dropwise at –30 °C. The obtained homogeneous mixture was allowed to warm up to room temperature, stirred for 1 h, and then used as a catalyst in ring opening polymerization (ROP) of heterocyclic monomers.

Polymerizations

The polymerizations were carried out in glass pressure reactors sealed by a screw with gasket on coupling, in dry nitrogen atmosphere. Solid monomers and compound **I** or **II** were placed in reactors in a nitrogen stream using glass adapters. Liquid monomers, solutions of catalysts or solvents were added by glass syringes with stainless steel needles. Bulk radical copolymerization of **I** with unsaturated monomers was initiated by MEKPO/CoEH redox system and carried out at 40 °C for 3 h. The obtained products were granulated and washed with acetone in a Soxhlet extractor in order to remove all unbound polymer. After that it was dried under vacuum at 50 °C for 2 days.

ATRP polymerization of styrene was carried out at 110 °C, in bulk or in toluene, in the presence of **II** and CuCl/bpy complex (with molar ratio of [St]:[(**II**)-Br]:[CuCl]:[bpy] = 100:1:1:2). After desired time the reaction mixture was dropped into stirred methanol. The unbound polystyrene was washed out of the solid raw product with cyclohexane and precipitated in methanol. The insoluble in cyclohexane solid residue was dispersed in toluene and treated with a mixture of water and trifluoroacetic acid to remove the inorganic core. The organic phase was shaken three times with water and evaporated. All the purified solid products were dried under vacuum at 50 °C for 2 days.

The polymerizations of heterocyclic monomers, with **III** as an initiator, were carried out in toluene at 25 °C or 60 °C, and a molar ratio of **III**/monomer equal to 0.02. In each case after a desired time the reactor was cooled, degassed, opened and then methylene chloride was added in order to dissolve raw products. The obtained solutions were shaken once with 5% hydrochloric acid to wash out the catalyst residue. Then, the organic phase was shaken with water three times and dropped into stirred methanol to precipitate the polymer (or the whole mixture was subjected to evaporation when nothing precipitated). The products were dried under vacuum at ca 50 °C for 2 days.

Results and Discussions

Radical copolymerization of I

Our preliminary studies[15] show that hybrid monomers obtained in the reaction of boehmite with acrylic or methacrylic acid do not copolymerize with vinyl monomers. It is probably due to the high degree of crystallinity of the formed basic aluminum carboxylate phases resulting in their poor miscibility and sedimentation in liquid organic compounds.[8] In order to diminish a fillers' tendency for crystalline phase formation and to increase their affinity for organic monomers, further work was limited only to **I**. This material contains ca. 36 wt% of boehmite, and the molar ratio of acrylate to laurate groups in basic aluminum dicarboxylate phase is 4.2:1. The presence of both types of carboxylate group, as well as unreacted boehmite is clearly indicated by FTIR spectrum of **I** (Figure 1a) in which one can observe absorption bands characteristic for alumoxane core (473, 617, 742 $\mathrm{cm^{-1}}$) and hydroxyl groups of boehmite (ν_{OH} at 3305 and 3095 $\mathrm{cm^{-1}}$, δ_{OH} at 1065 and 1156 $\mathrm{cm^{-1}}$), signals originating from stretching bands of carboxylate groups (ν_s at 1459 $\mathrm{cm^{-1}}$ and ν_{as} at 1579 $\mathrm{cm^{-1}}$), C=C stretching band of acrylate moiety at 1648 $\mathrm{cm^{-1}}$, C–H stretching bands of laurate ligand (2855 and 2926 $\mathrm{cm^{-1}}$) and stretching bands of hydroxyl groups forming basic aluminum carboxylate structure at 3675 $\mathrm{cm^{-1}}$.

Three main reflections ($2\theta = 14.6$, 28.4 and 38.6°) observed on XRD pattern of **I** (Figure 2a) originate from boehmite phase and the small intensity reflection at 2θ ca. 10.5°can be assigned to the crystalline phase of basic aluminum diacrylate,[8] which indicates that in this system boehmite phase is mainly covered with amorphous aluminum carboxylates.

The copolymerization experiments conducted for styrene or methyl methacrylate

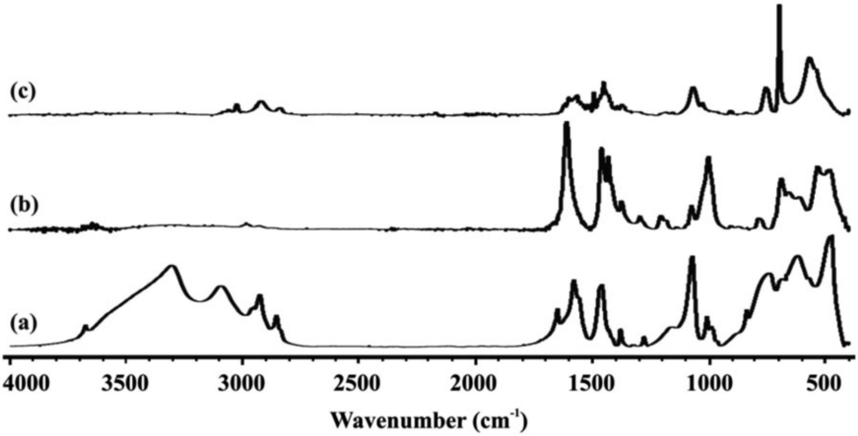


Figure 1.
FTIR spectra of: (a) carboxylate-alumoxane **I**, (b) carboxylate-alumoxane **II**, (c) polystyrene composite synthesized via ATRP method in the presence of **II** (3% of styrene conversion).

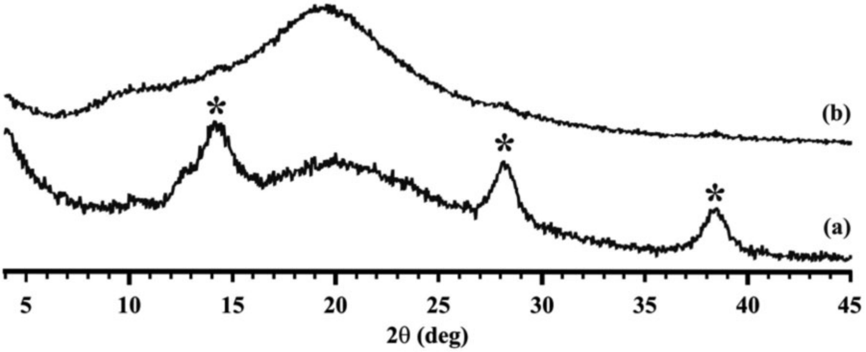


Figure 2.
XRD patterns of (a) carboxylate-alumoxane **I** and (b) cross-linked fraction of the product obtained in the copolymerization of styrene and **I**. * - signals of boehmite.

(Table 1) demonstrate that **I** can be a very effective curing agent. At 5 wt% content of **I** in the mixture with an appropriate monomer after 3 h of polymerization at 45 °C the vinyl monomer conversion is almost 100% and a cross-linked fraction constitutes 80–90% of the thus synthesized composite. On SEM image of the product prior to acetone extraction one can observe that the cross-linked phase forms irregular domains with dimensions in the range of 20–150 nm, uniformly dispersed in the composite, (Figure 3a). It contains also nanocrystallites of boehmite (see XRD patterns of cross-linked material Figure 2b), which constitute ca. 2 wt% of the whole composite. A high content of a cross-linked phase (82%) is also detected for vinyl acetate copolymerization product, but in this case the monomer conversion does not exceed 25% (Table 1). Probably it is due to the low resonance stabilization of vinyl acetate which consequently slows down the rate of its addition to the macroradicals terminated with aluminum acrylate monomeric units compared to styrene or methyl methacrylate.

We have conducted some experiments on the terpolymerization of **I** with maleic anhydride and styrene or oleic acid. It was found that these materials contain smaller

Table 1.
Radical copolymerization of carboxylate-alumoxane **I** [a].

Comonomer(s)	Comonomer(s) conversion (%) (%)	Crosslinked fraction (wt%)
styrene	~100	80
methyl methacrylate	~100	90
vinyl acetate	22	82
styrene/maleic anhydride [b]	~100	40
oleic acid/maleic anhydride [c]	~50	46

[a] 5 wt% of **I**, initiator: 2 wt% of MEKPO and 0.2 wt% of CoEH, temperature 40 °C, time 3 h. [b] styrene/maleic anhydride = 10:1 (mol/mol). [c] oleic acid/maleic anhydride = 1:1 (mol/mol).

amounts of the crosslinked phase (40–46%, Table 1) than binary systems. This observation is consistent with previous reports[16] indicating much lower reactivity of acrylic monomers during their addition to macroradicals terminated with donor monomeric units, compared to maleic anhydride. Nevertheless, these experiments clearly show that it is possible to synthesize a composite containing anhydride groups, which can be further functionalized. Boehmite content in cross-linked products of terpolymerization ranges from 4.5 to 7 wt%.

ATRP Polymerization of Styrene in the Presence of II

Elemental analysis of carboxylate-alumoxane **II** indicates that it contains ca. 90 wt% of basic aluminum 2-bromopropionate. SEM image (Figure 3b) shows the presence of fiber-like particles, which are typical for basic aluminum carboxylates with high degree of crystallinity.[8]

The polymerizations carried out in toluene at 110 °C lead to low yields: after 5–6 h of heating the styrene conversion is up to 3%, and practically all polymer is grafted on the hybrid matrix (there is no fraction

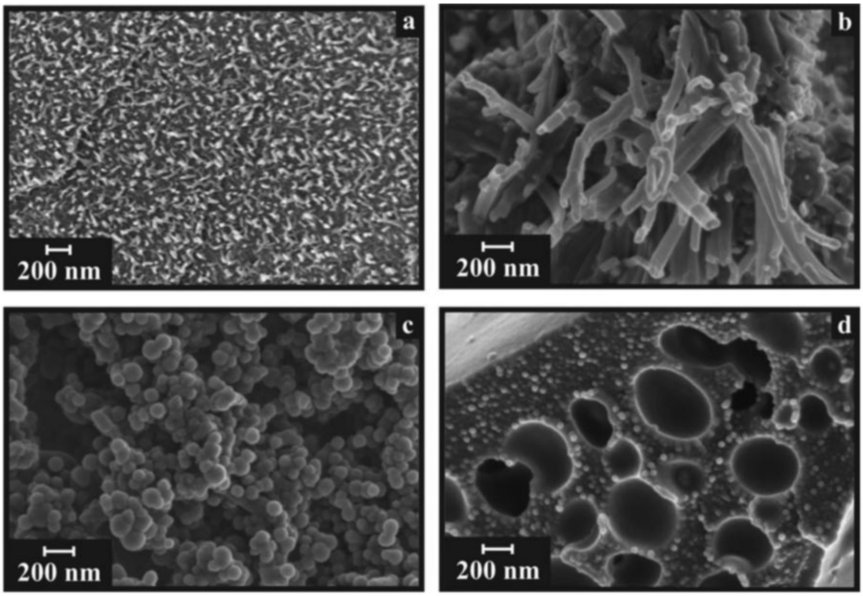
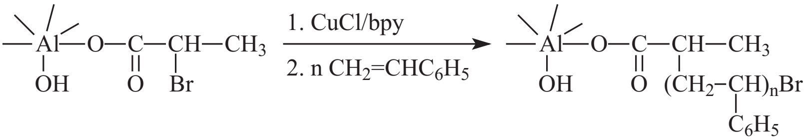


Figure 3.
SEM images of the product of styrene and **I** copolymerization (a), carboxylate- alumoxane **II** (b), and polystyrene composites synthesized via ATRP method in the presence of **II** at 3% (c) or 54% (d) of styrene conversion.

soluble in cyclohexane). SEM image of this grafted composite (Figure 3c) indicates, that during the reaction a fibrous structure of **II** is being destroyed and carboxylate-alumoxane surrounded by a polymer layer forms spherical particles with dimensions in the range of 200–300 nm. The initiation of ATRP polymerization should involve abstraction of bromine atom from 2-bromopropionate group followed by addition of styrene to the formed alkyl radical (Eq. 2).



$$-\mathrm{Al}(\mathrm{OH})-\mathrm{O}-\mathrm{C}(=\mathrm{O})-\mathrm{CH}(\mathrm{Br})-\mathrm{CH_3} \xrightarrow[2.\ n\ \mathrm{CH_2{=}CHC_6H_5}]{1.\ \mathrm{CuCl/bpy}} -\mathrm{Al}(\mathrm{OH})-\mathrm{O}-\mathrm{C}(=\mathrm{O})-\mathrm{CH}\big((\mathrm{CH_2{-}CH(C_6H_5)})_n\mathrm{Br}\big)-\mathrm{CH_3} \qquad (2)$$

This hypothesis is supported by FTIR spectra of composite (Figure 1c) in which one can determine two absorption bands originating from asymmetric stretching C=O vibrations of carboxylate ligand: the one with lower intensity (at 1617 cm^{-1}) can be assigned to 2-bromopropionate groups (in FTIR spectrum of **II** this band is located at 1611 cm^{-1}, Figure 1b), and the other with maximum at ca. 1565 cm^{-1} is within the range typical for aluminum salts of aliphatic carboxylic acids.[8]

At higher degrees of styrene conversion, apart from the grafted composite a fraction of thermally initiated polymer can be detected. This new phase forms a homogeneous matrix in which spherical particles of grafted composite are dispersed (Figure 3d). The size of dispersed particles decreases with monomer conversion probably due to better solubility of basic aluminum carboxylates grafted with longer polystyrene chains in organic continuous phase. At styrene conversion over 50%, the polymeric product precipitated in methanol easily forms stable colloidal dispersions in toluene or cyclohexane. The DLS analysis carried out for the former shows the presence of two populations of particles, with diameters within the range of 100–200 nm and 6–30 nm. In case of dispersion in cyclohexane, only a fraction of smaller particles (ca. 20 nm) is detected and it constitutes more than 95 wt% of a sample. The changes in molecular weights of polystyrene obtained after the removal of an inorganic core (Table 2) clearly indicates that the length of polymer chains increases with styrene conversion, with polydispersity indices between 1.3–1.6 – values typical for the ATRP systems with a significant contribution of thermal initiation.[17]

Polymerization of Heterocyclic Monomers Initiated by III

The results of our previous studies indicates that dihydroxyaluminum laurate, an intermediate product in the synthesis of **III**, forms colloidal dispersions in toluene with particle sizes from 7 to 12 nm.[18] It reacts with triethylaluminum to give products soluble in toluene. In ^{1}H NMR spectrum of **III** (Figure 4) there are 4 groups of signals corresponding to the alkyl substituent located in carboxylate ligand and 2 signals originating from alkyl groups bound to aluminum atoms. Protons of methyl groups

Table 2.
ATRP of styrene in the presence of carboxylate-alumoxane **II** [a)]

Time (h)	Solvent	Styrene conversion (%)	$M_n \times 10^{-3}$	M_w/M_n
5	toluene [b)]	2	2.5	1.4
6	toluene [b)]	3	2.6	1.6
24	toluene [b)]	–	4.4	1.3
48	toluene [b)]	18	5.1	1.4
24	bulk	24	8.4	1.6
48	bulk	54	17.0	1.4

[a)] molar ratio of reagents [St]:[(**II**)-Br]:[CuCl]:[bpy] = 100:1:1:2, temperature 110 °C. [b)] monomer concentration 0.8 g/ml.

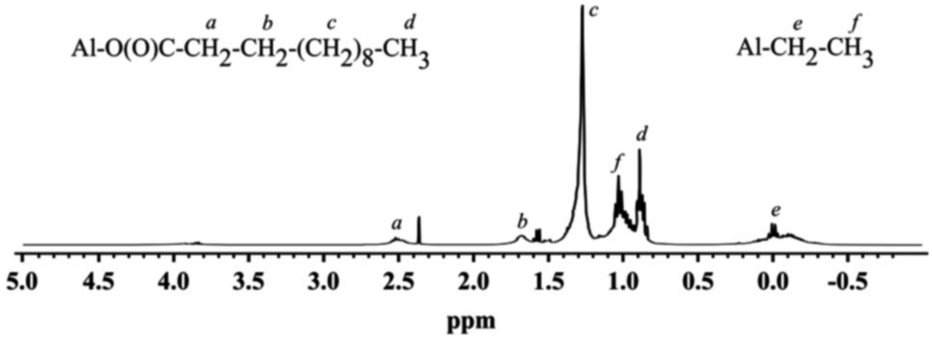
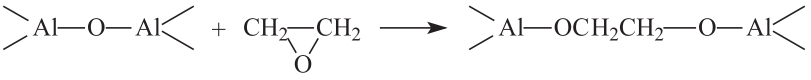


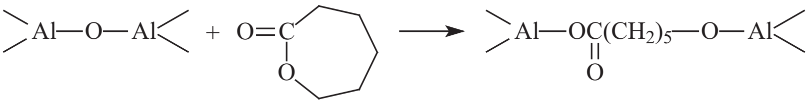
Figure 4.
^{1}H NMR spectrum of carboxylate-alumoxane **III**.

in these substituents form a series of multiplets with chemical shifts around 1 ppm, whereas methylene groups directly bound to aluminum give a broad band in the range of −0.2–0.0 ppm and a quartet at 0 ppm. Spectra of a similar type are observed in case of ethylalumoxanes, which are a mixture of oligomers containing [$Al(CH_2CH_3)O$] units complexed by some amount of triethylaluminum.[19] Although the exact structure of carboxylate-alumoxane **III** is still unidentified, there is no doubt that the alumoxane bridges [$Al{-}O{-}Al(C_2H_5)_2$] are present, which were formed in the reaction between Al−OH groups and triethylaluminum.

It was found that **III** initiates the polymerization of such heterocyclic monomers as ε- caprolactone (CL), trimethylene carbonate (TMC), propylene oxide (PO) or ethylene oxide (EO). Regardless of the choice of monomer all polymerizations proceed with rather high yields and polymeric products are characterized by Mn in the range of 1×10^4–5×10^4 and high polydispersity ($M_w/M_n \geq 1.9$) (Table 3).

Based on our previous work concerning coordination polymerization of heterocyclic monomers catalyzed by methylalumoxane[15] one can expect that in systems described in current work, polymerization proceeds on alkoxide active centers generated via monomer insertion into Al–O–Al bonds (Eq. 3 and 4). These bonds form highly associated structures difficult to penetrate for monomer molecules and the active centers occur relatively slowly in time during polymerization, which results in the observed high polydispersity of chain length.


(3)


(4)

For studied systems the molar ratio of monomer to the amount of $Al{-}O{-}Al(C_2H_5)_2$ bonds present in **III** was 25, but the average degrees of polymerization estimated by means of GPC are within the range of 100–400 for cyclic esters or 500–900 in the case of alkylene oxides. Therefore one can assume that the overwhelming part of alumoxane bonds is inactive in polymerization and creates oligomeric domains of carboxylate-alumoxane linked with each other by polymer

Table 3.
Polymerization of heterocyclic monomers initiated by **III** [a)]

Monomer	Temperature (°C)	Time (h)	Yield (%)	$M_n \times 10^{-3}$	M_w/M_n
CL	60	1	46	10.0	1.9
		24	98	42.0	2.1
TMC PO	60	1	94	10.1	1.9
	60	1	80	32.0	2.8
EO	25	24	90	52.0	2.6
		24	96	22.2	>5

[a)] toluene as a solvent, molar ratio of monomer/initiator = 25.

segments. This explanation is also supported by the fact that after a short period of time in all the polymerized systems the formation of transparent gels is observed. They can be destroyed by addition of methanol, water or acids and organic polymers can be isolated by extraction. After the addition of water the systems based on poly(ethylene oxide) generate a stable dispersion of filler particles (diameters between 0.2 and 1.5 μm) in polymer solution, which upon water evaporation transforms into solid composites containing ca. 20 wt% of aluminum carboxylates. The dispersion of these materials in polar solvents (e.g. methylene chloride or acetonitrile) provides a convenient method for the synthesis of composites with other organic polymers.

Conclusion

Reactions of boehmite with acrylic and lauric acids are a very simple and efficient way for synthesis of reactive fillers which can act as curing agents in radical polymerizations, e.g. cross-linking of unsaturated polyester resins. Carboxylate-alumoxanes obtained in the reaction with carboxylic acids containing active sites or atoms can be used for preparation of nanocomposites using the *in situ* ATRP method. As a result of these processes, polymers grafted in the form of nanospheres which can be dispersed in the matrix of organic polymer are being obtained. It is necessary, however, to verify the effectiveness of this method through the selection of more active ATRP catalyst, testing a wider range of monomers and examining the influence of the addition of nanoparticles on functional properties of their composites with different organic polymers. Basic aluminum carboxylates in the reaction with triethylaluminum create alumoxanes able to initiate processes of the polymerization of some heterocyclic monomers. As a result of these reactions it is possible to obtain gels or solid mixtures of aluminum carboxylates in polymer matrices with high efficiency. From a practical point of view the composites of aluminum carboxylates with poly(ethylene oxide) seem to be interesting since it is possible to use them for the preparation of solid polymer electrolytes providing fast transport of lithium cations.[20] However, it is not a good method of synthesis of pure polymers, because of the high polydispersity of macromolecules and the difficulties with the catalyst residue removal.

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