Metal acetylacetonate–amine and metal nitrate–amine complexes as low-emission catalysts for rigid polyurethane foam preparation

Duangruthai Sridaeng,[1] Alisa Limsirinawa,[2] Piyachat Sirojpornphasut,[3] Siriwan Chawiwannakorn,[3] Nuanphun Chantarasiri[2]

[1]Department of Chemistry, Faculty of Science, Rangsit University, Pathumthani 12000, Thailand
[2]Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[3]Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
Correspondence to: N. Chantarasiri (E‐mail: nuanphun.c@chula.ac.th)

ABSTRACT: Six metal–amine complexes, $Cu(acac)_2(trien)$, $Zn(acac)_2(en)$, $Zn(acac)_2(trien)$, $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2(trien)$, and $Cu(NO_3)_2(tetraen)$, are synthesized from metal acetylacetonates [$M(acac)_2$, where M = Cu and Zn] or metal nitrate [$M(NO_3)_2$, where M = Cu] and aliphatic amines (en = ethylenediamine, trien = triethylenetetramine, and tetraen = tetraethylenepentamine). These metal–amine complexes can be used as catalysts in the preparation of rigid polyurethane (RPUR) foams. All metal–amine complexes emit very weak odor when compared with N,N-dimethylcyclohexylamine (DMCHA), which is a commercial catalyst commonly used in the preparation of RPUR foams. DMCHA emits very strong amine odor that affects working environment in RPUR foam processing. Among all metal complexes, $Cu(acac)_2(trien)$ has the highest catalytic activity. In comparison with DMCHA, $Cu(acac)_2(trien)$ shows slightly higher catalytic activity in gelling reaction but lower catalytic activity in blowing reaction. RPUR foam prepared from $Cu(acac)_2(trien)$ has lower density and compressive strength than that prepared from DMCHA. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42332.

INTRODUCTION

Rigid polyurethane (RPUR) foams are one of the most versatile polymers that are mainly used as insulation materials. RPUR foam is prepared by the reaction of a polyol with a diisocyanate or a polymeric isocyanate in the presence of suitable catalyst, surfactant, blowing agent, and other additives.[1,2] Tertiary amines and tin compounds are mainly used as catalysts for polyurethane formation, for example, dibutyltin dilaurate (DBTDL), stannous octoate, N,N-dimethylcyclohexylamine (DMCHA), and triethylenediamine. However, tin is toxic and amine emits strong odor. Therefore, the development of new catalysts is a topic of interest.

Metal acetylacetonates [$M(acac)_2$] are widely used in many organic and polymerization reactions. The attractiveness of these metal acetylacetonates is due to their solubility in organic solvents, long shelf-life, and stability in air. $Cu(acac)_2$ is an inexpensive catalyst which can be used in many types of reactions, for example, oxidative C—H bond amination of azoles with amines[3] and polycondensation of bis(diazoacetate)s

to give a well-defined unsaturated polyesters.[4] $Zn(acac)_2$ is used as an initiator for ring-opening polymerization in the synthesis of high-molecular-weight polycarbonates,[5] catalyst for chain extension of polyesters,[6] and latent accelerator for anhydride-cured epoxy resins.[7] $Co(acac)_3$ can be used as a catalyst in the synthesis of styrene–acrylonitrile copolymers[8] and initiator for graft copolymerization of 4-vinylpyridine onto cellulose.[9]

As metal acetylacetonates are less toxic than tin compounds, they can be used as catalysts in the synthesis of polyurethane to replace tin catalysts. Cobalt(II) hexafluoroacetylacetonate–cobalt(II) acetylacetonate [$Co(f_6acac)_2$–$Co(acac)_2$] system can catalyze the polymerization between isophorone diisocyanate and diethylene glycol with higher catalytic activity than DBTDL.[10] $Zr(acac)_4$ is a catalyst in the synthesis of isophorone diisocyanate-based waterborne polyurethanes.[11–13] When $Zr(acac)_4$–triethylamine system is used, its catalytic activity is comparable with that of dibutyltin diacetate.[13] Polymerization reaction of hexamethylene diisocyanate with diethylene glycol can be catalyzed by $M(acac)_2$–triethylenediamine system (M = Mn, Fe, Co,

Ni, and Cu)[14] and Mn(acac)$_2$–triethylenediamine system has comparable catalytic activity with that of DBTDL.

Copper(II) nitrate is used as an oxidizing and a nitrating agent in organic chemistry. Tris(3,5-dimethylpyrazole)copper(II) nitrate is used as a catalyst for mild oxidation of organic substrates.[15] In the presence of molecular oxygen as an oxidant, copper(II)–sparteine complexes with chelating nitrate ligand are used as catalyst for oxidation of benzyl alcohol to benzoic acid and cyclohexanol to cyclohexanone.[16] The combination of copper(II) nitrate and bipyridine ligands gives active catalyst for oxidative coupling of 2,6-dimethylphenol.[17]

From the previous work in our group, copper acetate–ethylenediamine complex [Cu(OAc)$_2$(en)$_2$] was synthesized from the reaction between copper acetate [Cu(OAc)$_2$] and ethylenediamine (en).[18] Cu(OAc)$_2$(en)$_2$ can be used as a catalyst in RPUR foam preparation and shows comparable catalytic activity with the commercial catalyst (DMCHA). However, the rise profile of Cu(OAc)$_2$(en)$_2$ is slow in the initial stage and then becomes very fast in the middle stage. This exothermic reaction in the middle stage may result in accumulation of heat in a short time and causes foam degradation during the foam formation. Cu(OAc)$_2$(en)$_2$ also has fast gel time. Therefore, preparation of RPUR foam specimen having large dimension will be difficult. To solve this problem, the catalysts having slightly lower reactivity than Cu(OAc)$_2$(en)$_2$ were prepared. As amine is known to act as cocatalyst for M(acac)$_2$ in the reaction between hexamethylene diisocyanate and diethylene glycol to give polyurethane,[14] we were interested to synthesize metal acetylacetonate–amine and metal nitrate–amine complexes from the reaction between metal salts and aliphatic amines. The metal salts used were Cu(acac)$_2$, Zn(acac)2, and Cu(NO$_3$)$_2$. The amines used were ethylenediamine (en), triethylenetetramine (trien), and tetraethylenepentamine (tetraen). Six metal complexes, Zn(acac)$_2$(en), Cu(acac)$_2$(trien), Zn(acac)$_2$(trien), Cu(NO$_3$)$_2$(en)$_2$, Cu(NO$_3$)$_2$(trien), and Cu(NO$_3$)$_2$(tetraen), were synthesized and used as catalysts for RPUR foam preparation. These metal–amine complexes could be easily prepared from readily available starting materials. They are stable in air, have very weak odor, and have good solubility in the starting materials used in the preparation of RPUR foam. Therefore, the metal acetylacetonate–amine and metal nitrate–amine complexes are other alternative catalysts for RPUR foam preparation. The obtained results in RPUR foam preparation using the synthesized catalysts were compared with those obtained from DMCHA.

EXPERIMENTAL

Materials

Copper(II) acetylacetonate [Cu(acac)$_2$], zinc(II) acetylacetonate hydrate [Zn(acac)$_2$·xH$_2$O], copper(II) nitrate trihydrate [Cu(NO$_3$)$_2$·3H$_2$O], ethylenediamine (en), triethylenetetramine (trien), and tetraethylenepentamine (tetraen) were obtained from TCI and Aldrich. Distilled water was used as a blowing agent. Polymeric 4,4′-methane diphenyl diisocyanate (PMDI, Suprasec® 5005, % NCO = 31.0 wt %, average functionality = 2.7), polyol (Daltolac® 180, sucrose-based polyether polyol, hydroxyl value = 440 mg of KOH/g, functionality = 4.3),

polysiloxane surfactant (Tegostab® B8460), and DMCHA were supplied by Huntsman (Thailand) Co. Ltd.

Experimental Design

Six metal–amine complexes were synthesized and used as catalysts in the preparation of RPUR foams. Isocyanate index of 100 was used in RPUR foam formulation. RPUR foams were prepared using two methods, namely, cup test and molded methods. The amounts of all components in RPUR foam formulation were kept constant. By using different metal–amine complexes as catalysts, reaction times in the preparation of RPUR foams and RPUR foam properties were investigated. The results were compared with those obtained from DMCHA, which was used as a reference catalyst.

Measurements

Characterization of Metal–Amine Complexes. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer RX I FTIR spectrometer over the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. Ultraviolet–visible (UV–vis) spectra were recorded on a Varian Cary 50 UV–vis spectrophotometer over the range 200–500 nm at a medium speed. The metal content was analyzed with a Perkin-Elmer AAnalyst 100 atomic absorption spectrometer. Elemental analysis (CHN) was carried out using a Perkin-Elmer EP 2400 analyzer. MALDI-TOF mass spectra were carried out using Bruker Daltonics mass spectrometer, and 2-cyano-4-hydroxy cinnamic acid was used as a matrix.

Characterization of RPUR Foams. The reaction times, namely, cream time (the time when the foam started to rise which was taken at 5% foam height when compared with the total height), gel time (the time when the foam mixture started to appear as gel), tack-free time (the time when polymerization reaction was completed which could be observed by the dryness of foam surface), and rise time (the time when the foam stopped rising) were recorded using a digital stopwatch. The foam height was recorded as the height of foam prepared using cup test method. The height of DMCHA was designated as 100%. The height of the other foams was calculated in relation to that of DMCHA. For example, if the height of DMCHA was 16 cm, the foam having the height of 14.8 cm was designated as 93% height. Rise profiles were obtained by measuring height of foams prepared by cup test method at different reaction times. Isocyanate conversion was obtained from attenuated total reflection infrared (ATR–IR) spectra, which were recorded on a Nicolet 6700 FTIR spectrometer over the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. The density of the foams was measured according to ASTM D-1622-09. The size of specimen was 3.0 × 3.0 × 3.0 cm^3. The average values of three samples are reported. The morphology of the foams in parallel and perpendicular to the foam-rising direction was studied with a Hitachi S-4800 scanning electron microscope. The samples were gold coated before scanning, and the accelerating voltage was 20 kV. Compression testing of the foams in parallel and perpendicular to the foam-rising direction was performed with a Lloyd LRX universal testing machine according to ASTM D-1621-09. For compression tests, the specimens were cut into a cubic shape with dimensions of 3.0 × 3.0 × 3.0 cm^3. The cross section of the specimens was 9.0 cm^2, which was less than that recommended by

ASTM (25.8 cm^2). The rate of crosshead movement was fixed at 2.54 mm/min, and the preload cell used was 0.100 N. Compressive strength was measured by plotting applied force (compressive strength) against deformation of the foam sample (compressive strain), and the data were recorded at 10% deformation.

General Procedure for the Synthesis of Metal–Amine Complexes

A solution of amine in methanol was stirred at room temperature. Metal acetylacetonate or metal nitrate was added to the amine solution. After the reaction mixture was stirred at room temperature overnight, metal–amine complex precipitated from the solution. The precipitate was isolated by filtration, washed with methanol, and dried *in vacuo*. For metal–amine complex which was isolated as liquid product, the reaction mixture was evaporated and dried *in vacuo* to remove methanol.

Synthesis of Copper Acetylacetonate-Triethylenetetramine Complex [Cu(acac)$_2$(trien)].

Copper(II) acetylacetonate (0.642 g, 2.45 mmol), triethylenetetramine (0.37 mL, 2.45 mmol), and methanol (25 mL) were used in the synthesis. Cu(acac)$_2$(trien) was obtained as a blue viscous liquid (0.972 g, quantitative) and was used without further purification: IR (KBr): v = 3450 (m; N—H), 2931 (w; C—H), 1584 (s; v_{as} C=O), 1531 (s; v_s C=O), 1350 (m; C—N), 1018 cm^{-1} (m; C—O); UV–vis (MeOH); λ_{max} (ε) = 273 nm (5220); MS (MALDI-TOF, m/z): [Cu(acac)$_2$(trien)]$^+$ calcd for CuC$_{16}$H$_{32}$N$_4$O$_4$, 407.17; found, 408.51. [Cu(acac)$_2$(trien) + H$_2$O]$^+$ calcd for CuC$_{16}$H$_{34}$N$_4$O$_5$, 425.18; found, 426.37. [Cu(acac)$_2$(trien) + H$_2$O + Na]$^+$ calcd for NaCuC$_{16}$H$_{34}$N$_4$O$_5$, 448.17; found, 449.38.

Synthesis of Zinc Acetylacetonate-Ethylenediamine Complex [Zn(acac)$_2$(en)].

Zinc(II) acetylacetonate (0.687 g, 2.60 mmol), ethylenediamine (0.35 mL, 5.20 mmol), and methanol (25 mL) were used in the synthesis. Zn(acac)$_2$(en)[19] was isolated by filtration, washed with methanol, and dried *in vacuo*. Zn(acac)$_2$(en) was obtained as a white powder (0.791 g, 79%): IR (KBr): v = 3318 (m; N—H), 2972 (w; C—H), 1602 (s; v_{as} C=O), 1507 (s; v_s C=O), 1320 (m; C—N), 1124 cm^{-1} (m; C—O); UV–vis (MeOH); λ_{max} (ε) = 288 nm (980); MS (MALDI-TOF, m/z): [Zn(acac)$_2$(en)]$^+$ calcd for ZnC$_{12}$H$_{22}$N$_2$O$_4$, 323.70; found, 323.05; Anal. calcd. for ZnC$_{12}$H$_{22}$N$_2$O$_4$ [Zn(acac)$_2$(en)]: C, 44.52; H, 6.85; N, 8.65; Zn, 20.20; found: C, 44.50; H, 7.31; N, 8.74; Zn, 20.16.

Synthesis of Zinc Acetylacetonate-Triethylenetetramine Complex [Zn(acac)$_2$(trien)].

Zinc(II) acetylacetonate (0.643 g, 2.44 mmol), triethylenetetramine (0.36 mL, 2.44 mmol), and methanol (25 mL) were used in the synthesis. Zn(acac)$_2$(trien) was obtained as a yellow viscous liquid (0.985 g, quantitative) and was used without further purification: IR (KBr): v = 3300 (m; N—H), 2978 (w; C—H), 1616 (s; v_{as} C=O), 1504 (s; v_s C=O), 1323 (m; C—N), 1127 cm^{-1} (m; C—O); UV–vis (MeOH); λ_{max} (ε) = 278 nm (1125); MS (MALDI-TOF, m/z): [Zn(acac)$_2$(trien) + 2H + Na]$^+$ calcd for NaZnC$_{16}$H$_{34}$N$_4$O$_4$, 433.18; found, 434.41.

Synthesis of Copper Nitrate-Ethylenediamine Complex [Cu(NO$_3$)$_2$(en)$_2$].

Copper(II) nitrate trihydrate (0.33 g, 1.38 mmol), ethylenediamine (0.19 mL, 2.85 mmol), and methanol

Table I. RPUR Foam Formulations (in Parts by Weight Unit, pbw)

Chemicals	pbw
Polyol (Daltolac® 180)	100
Catalysts (metal–amine complexes or DMCHA)	1.0
Surfactant (Tegostab® B8460)	2.5
Blowing agent (H$_2$O)	3.0
Polymeric MDI (PMDI; Suprasec® 5005)	151

(10 mL) were used in the synthesis. Cu(NO$_3$)$_2$(en)$_2$ was obtained as a purple powder (0.49 g, 93%): IR (KBr): v = 3156 (m; N—H), 2886 (w; C—H), 1454 (s; v_{as} N—O), 1336 cm^{-1} (s; v_s N—O); UV–vis (MeOH); λ_{max} (ε) = 207 nm (4890); MS (MALDI-TOF, m/z): [Cu(NO$_3$)$_2$(en)$_2$]$^+$ calcd for CuC$_4$H$_{16}$N$_6$O$_6$, 307.04; found, 308.06; Anal. calcd. for CuC$_4$H$_{16}$N$_6$O$_6$ [Cu(NO$_3$)$_2$(en)$_2$]: C, 15.61; H, 5.24; N, 27.31; found: C, 16.05; H, 5.87; N, 27.57.

Synthesis of Copper Nitrate-Triethylenetetramine Complexes [Cu(NO$_3$)$_2$(trien)].

Copper (II) nitrate trihydrate (0.31 g, 1.28 mmol), triethylenetetramine (0.19 mL, 1.27 mmol), and methanol (10 mL) were used in the synthesis. Cu(NO$_3$)$_2$(trien) was obtained as a blue viscous liquid (0.41 g, quantitative): IR (KBr): v = 3233 (m; N—H), 2881 (w; C—H), 1454 (s; v_{as} N—O), 1304 cm^{-1} (s; v_s N—O); UV–vis (MeOH); λ_{max} (ε) = 210 nm (3540); MS (MALDI-TOF, m/z): [Cu(NO$_3$)$_2$(trien)]$^+$ calcd for CuC$_6$H$_{18}$N$_6$O$_6$, 333.06; found, 334.29.

Synthesis of Copper Nitrate-Tetraethylenepentamine Complexes [Cu(NO$_3$)$_2$(tetraen)].

Copper(II) nitrate trihydrate (0.551 g, 2.28 mmol), tetraethylenepentamine (0.46 mL, 2.41 mmol), and methanol (10 mL) were used in the synthesis. Cu(NO$_3$)$_2$(tetraen) was obtained as a dark blue powder (0.86 g, 86%): IR (KBr): v = 3207 (m; N—H), 2939 (w; C—H), 1509 (s; v_{as} N—O), 1431 cm^{-1} (s; v_s N—O); UV–vis (MeOH); λ_{max} (ε) = 265 nm (8125); MS (MALDI-TOF, m/z): [Cu(NO$_3$)$_2$(tetraen) + H$_2$O + K$^+$] calcd for KCuC$_8$H$_{25}$N$_7$O$_7$, 433.07; found, 433.57.

Preparation of RPUR Foams Using Cup Test Method

RPUR foam was prepared using a two-step method. In the first mixing step, polyol, catalysts (metal acetylacetonate–amine complexes, metal nitrate–amine complexes or DMCHA), surfactant, and blowing agent (water) were mixed in a 700-mL paper cup. In the second mixing step, PMDI was added to the mixed polyol from the first mixing step, and then, the mixture was mixed by a mechanical stirrer at 2000 rpm for 20 s. The foam was allowed to rise freely. During the foaming reaction, cream time, gel time, tack-free time, and rise time were measured. After that, the foams were kept at room temperature for 48 h before further characterizations. The foam height and density were measured. Isocyanate conversion was determined by ATR-IR spectroscopy.

RPUR foams were prepared at the NCO index of 100 (Table I). NCO index is a measure of excess isocyanate used relative to the theoretical equivalent amount required to react with polyol
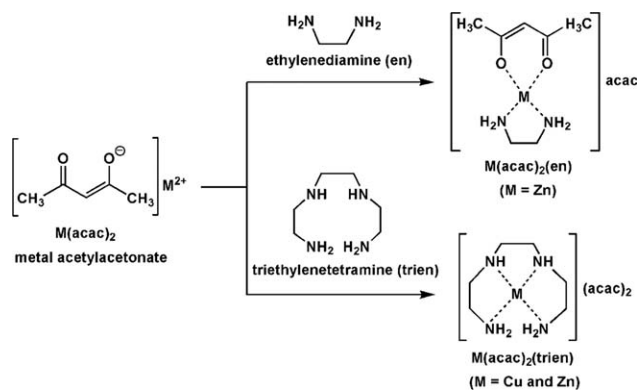
Scheme 1. Synthesis of metal acetylacetonate–amine complexes.

and blowing agent (water). Isocyanate index is determined using the following equation:

NCO Index = (Actual amount of isocyanate used/

Theoretical amount of isocyanate) ×100.

From Table I, parts by weight (pbw) is used as the unit in foam formulations. Parts by weight is the weight of components (in grams) per 100 g of polyol. For example, when 100 g of polyol is used at the NCO index of 100, the weight of catalyst, surfactant, blowing agent (water), and polymeric MDI used in this formulation are 1.0, 2.5, 3.0, and 151 g, respectively.

RPUR foams obtained from different catalysts have similar IR absorptions as follows: IR (ATR-IR): v = 3320 (m; N—H), 2907 (m; C—H), 2874 (m; C—H), 2272 (w; free NCO), 1711 (s; C═O), 1595 (m; Ar-H), 1075 cm^{-1} (s; C—O urethane).

Preparation of RPUR Foams in the Mold
RPUR foams were prepared by mixing all starting materials in a paper cup and poured into a 10.0 × 10.0 × 10.0 cm^3 plastic mold. The foam was allowed to rise freely, and after the foaming reaction was completed, it was kept at room temperature for 48 h before further characterizations of physical and mechanical properties, namely, density, morphology, and compressive strength. RPUR foams prepared in a mold have the same density as those prepared using cup test method.

RESULTS AND DISCUSSION

Synthesis and Characterization of Metal Acetylacetonate–Amine Complexes
The reactions between metal acetylacetonates and aliphatic amines to give metal acetylacetonate–amine complexes are shown in Scheme 1. The reaction between zinc acetylacetonate and ethylenediamine gave zinc–ethylenediamine complex [Zn(acac)$_2$(en)]. IR spectrum of Zn(acac)$_2$(en) shows asymmetric and symmetric C═O stretching at 1602 and 1507 cm^{-1}, respectively. These C═O peaks are different from those of Zn(acac)$_2$, which appear at 1593 cm^{-1} (asymmetric C═O) and 1514 cm^{-1} (symmetric C═O). The λ_{max} of Zn(acac)$_2$(en) in UV spectrum is similar to that of Zn(acac)$_2$. Both IR and elemental analysis data agreed with the previous work.[19] In addition, MALDI-TOF mass spectrometry data of Zn(acac)$_2$(en) show the peak of [Zn(acac)$_2$(en)]$^+$ at m/z = 323.05, which indicate that its molecular formula is Zn(acac)$_2$(en).

Copper and zinc acetylacetonate underwent reactions with triethylenetetramine to give products as viscous liquids, which could be used in RPUR foam preparation without purification. The products obtained from copper and zinc acetylacetonate were proposed to be Cu(acac)$_2$(trien) and Zn(acac)$_2$(trien), respectively. IR spectrum of Cu(acac)$_2$(trien) [Figure 1(a)] exhibits asymmetric and symmetric C═O stretching at 1584 and 1531 cm^{-1}, respectively. These C═O stretching bands are different from those of Cu(acac)$_2$, which appear at 1575 cm^{-1} (asymmetric C═O) and 1522 cm^{-1} (symmetric C═O). Zn(acac)$_2$(trien) shows asymmetric and symmetric C═O stretching at 1616 and 1504 cm^{-1}, respectively, which are different from those of Zn(acac)$_2$ [Figure 1(b)]. UV–visible spectrum of Cu(acac)$_2$(trien) shows λ_{max} at 273 nm, which shifts from that of Cu(acac)$_2$ at 292 nm [Figure 2(a)]. In addition, the λ_{max} of Zn(acac)$_2$(trien) at 278 nm slightly shifts from that of Zn(acac)$_2$ at 285 nm [Figure 2(b)]. MALDI-TOF mass spectrometry gives the peak of Cu(acac)$_2$(trien) at m/z = 408.51 [Figure 3(a)]. Other two peaks appear at m/z = 426.37 and 449.38, which correspond to [Cu(acac)$_2$(trien) + H$_2$O]$^+$ and [Cu(acac)$_2$(trien) + H$_2$O + Na]$^+$, respectively. Zn(acac)$_2$(trien) gives m/z at 434.41, which corresponds to [Zn(acac)$_2$(trien) + 2H + Na]$^+$ [Figure 3(b)].

There are reports on the X-ray structures of copper complexes of the type [Cu(acac)(NN)X], where NN is an amine and X is an anion,[20–22] for example, [Cu(acac)(phen)(NO$_3$)]·H$_2$O and
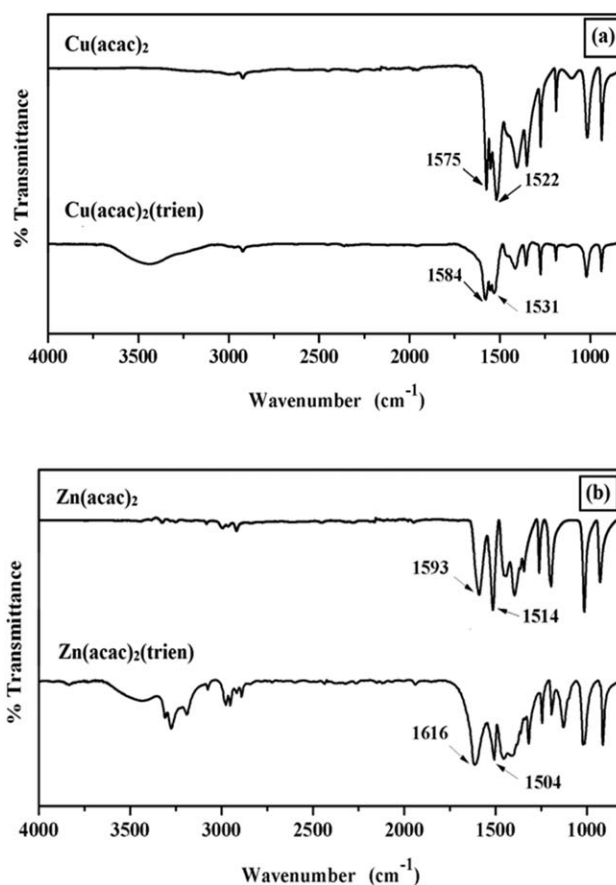
Figure 1. IR spectra of (a) Cu(acac)$_2$ and Cu(acac)$_2$(trien) and (b) Zn(acac)$_2$ and Zn(acac)$_2$(trien).
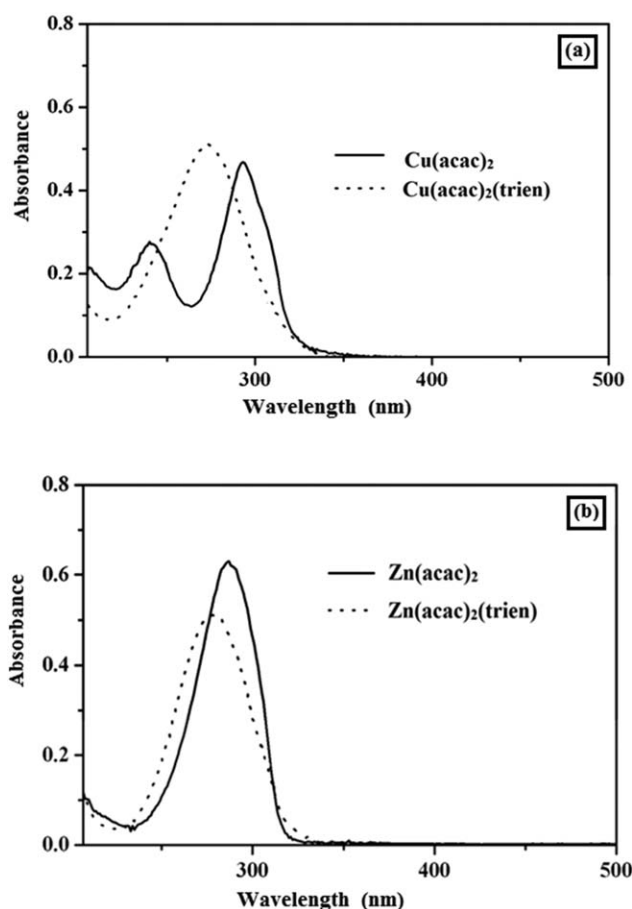
Figure 2. UV spectra of (a) Cu(acac)$_2$ and Cu(acac)$_2$(trien) and (b) Zn(acac)$_2$ and Zn(acac)$_2$(trien).

Figure 3. MALDI-TOF mass spectra of (a) Cu(acac)$_2$(trien) and (b) Zn(acac)$_2$(trien). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Cu(acac)(dmph)(NO$_3$)], where acac = acetylacetonate, phen = 1,10-phenanthroline, and dmph = 2,9-dimethyl-1,10-phenanthroline.[20] Copper atom in both complexes has an approximate square pyramidal coordination geometry with two nitrogen atoms (both from phen or dmph) and three oxygen atoms (two from acac and one from NO$_3^-$ as counter ion).

Therefore, it was proposed that the liquid products obtained from copper and zinc acetylacetonate were Cu(acac)$_2$(trien) and Zn(acac)$_2$(trien), respectively. The structure of Cu(acac)$_2$(trien) was proposed to have a similar structure to [Cu(acac)(phen)-(NO$_3$)]·H$_2$O and [Cu(acac)(dmph)(NO$_3$)] as shown in Scheme 1. Zn(acac)$_2$(trien) structure was proposed to be the same as that of Cu(acac)$_2$(trien).

Similar to the synthesis of metal acetylacetonate–amine complexes, the reactions between metal nitrates and aliphatic amines give metal nitrate–amine complexes as shown in Scheme 2. IR spectrum of Cu(NO$_3$)$_2$(en)$_2$ exhibits N—O stretching of nitro group at 1454 cm^{-1} (asymmetric N—O) and 1336 cm^{-1} (symmetric N—O). These absorptions are different from those of Cu(NO$_3$)$_2$ absorption bands, which appear around at 1507 cm^{-1} (asymmetric N—O) and 1432 cm^{-1} (symmetric N—O). IR peaks of Cu(NO$_3$)$_2$(trien) and Cu(NO$_3$)$_2$(tetraen) also shift from those of Cu(NO$_3$)$_2$. These data suggested that

the complexes were formed. UV–visible spectra of copper nitrate–amine complexes show the maximum absorption of Cu(NO$_3$)$_2$(en)$_2$, Cu(NO$_3$)$_2$(trien), and Cu(NO$_3$)$_2$(tetraen) at
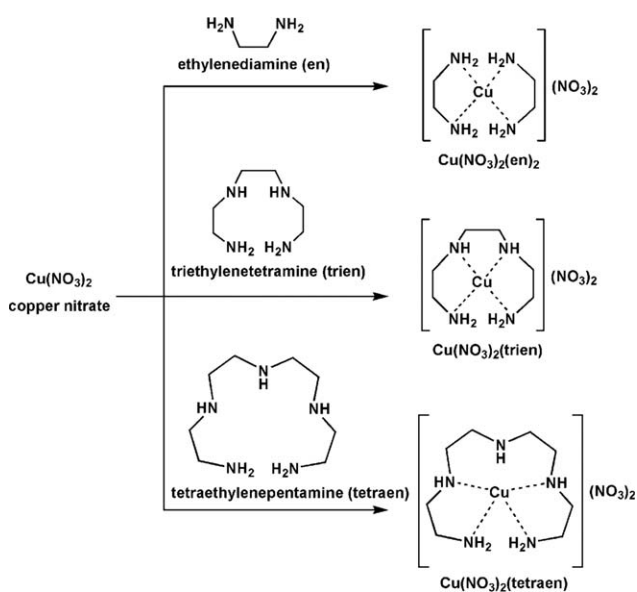
Scheme 2. Synthesis of metal nitrate–amine complexes.

Table II. Reaction Times and Physical and Mechanical Properties of RPUR Foams Prepared at NCO Index of 100 Catalyzed by Metal–Amine Complexes[a]

Catalyst	Cream time (s)	Gel time (s)	Tack-free time (s)	Rise time (s)	Density (kg/m^3)	Foam height[b] (%)	Compressive strength (kPa)	
							Parallel	Perpendicular
DMCHA	22	32	187	141	39.7	100	356.4	297.1
Cu(acac)$_2$(trien)	26	66	145	158	38.0	93	291.9	258.3
Zn(acac)$_2$(en)	30	93	366	301	39.0	81	333.8	317.2
Zn(acac)$_2$(trien)	25	62	229	182	35.5	93	265.3	201.9
Cu(NO$_3$)$_2$(en)$_2$	83	172	282	295	44.9	75	222.1	187.3
Cu(NO$_3$)$_2$(trien)	53	200	378	528	46.6	63	356.8	293.8
Cu(NO$_3$)$_2$(tetraen)	30	183	705	820	45.8	75	294.5	214.1

[a] The data reported are average values with standard deviation less than 5% from the average values.
[b] DMCHA gave the highest foam height and was designated as 100%.

207, 210, and 265 nm, respectively. These peaks shift from that of Cu(NO$_3$)$_2$, which appears at 205 nm. These results suggested the complex formation. MALDI-TOF mass spectra of Cu(NO$_3$)$_2$(en)$_2$, Cu(NO$_3$)$_2$(trien), and Cu(NO$_3$)$_2$(tetraen) give the molecular ion peaks at $m/z = 308.06$, 334.29, and 433.57, respectively, which correspond to [Cu(NO$_3$)$_2$(en)$_2$]$^+$, [Cu(NO$_3$)$_2$(trien)]$^+$, and [Cu(NO$_3$)$_2$(tetraen) + H$_2$O + K$^+$], respectively. Based on these data, the structure of metal acetylacetonate–amine complexes was proposed to be Cu(NO$_3$)$_2$(en)$_2$, Cu(NO$_3$)$_2$(trien), and Cu(NO$_3$)$_2$(tetraen).

Preparation of RPUR Foams Catalyzed by Metal Acetylacetonate–Amine Complexes

The reaction time of RPUR foam catalyzed by metal acetylacetonate–amine complexes is shown in Table II. The data reported are average values with standard deviation less than 5% from the average values. The catalytic activity in gelling reaction, which is the reaction between isocyanate and hydroxyl groups of polyols to form urethane groups, was determined by tack-free time of the catalyst. It was found that among all metal complexes, Cu(acac)$_2$(trien) had the best catalytic activity and had slightly higher catalytic activity in gelling reaction than DMCHA as Cu(acac)$_2$(trien) gave shorter tack-free time than DMCHA. Zn(acac)$_2$(en) and Zn(acac)$_2$(trien) had lower catalytic activity in gelling reaction than DMCHA. Zn(acac)$_2$(en) had the lowest activity because it contains only one ethylenediamine unit.
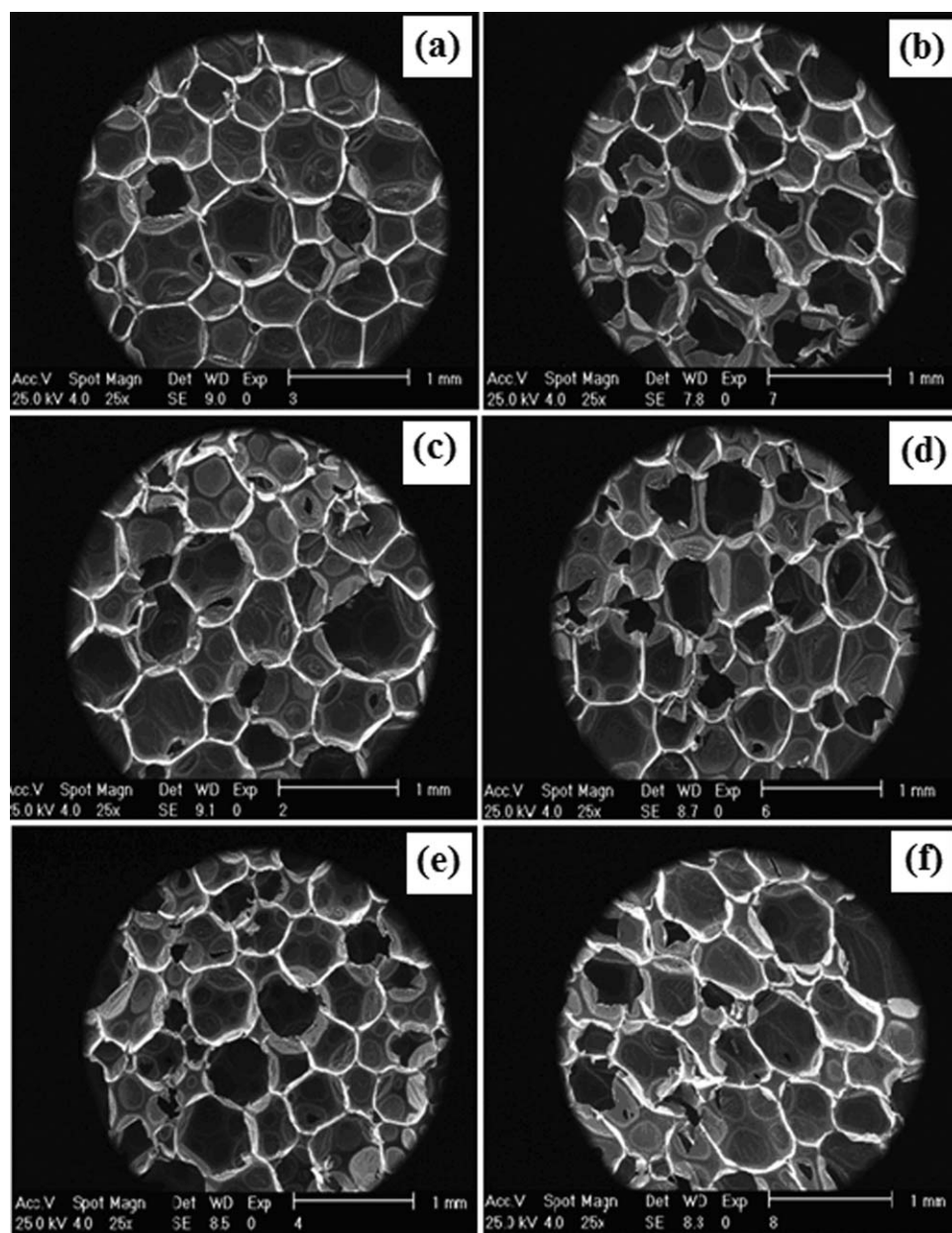
Rise time and rise profile indicate the catalytic activity in blowing reaction, which is the reaction between isocyanate and
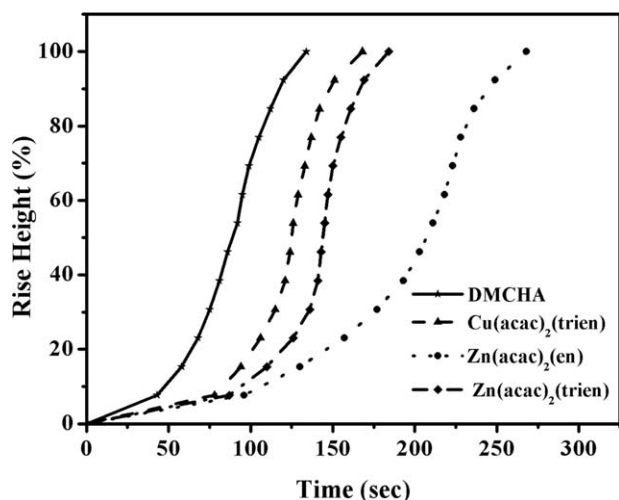
Figure 4. Rise profile of RPUR foams prepared from metal acetylacetonate–amine complexes.
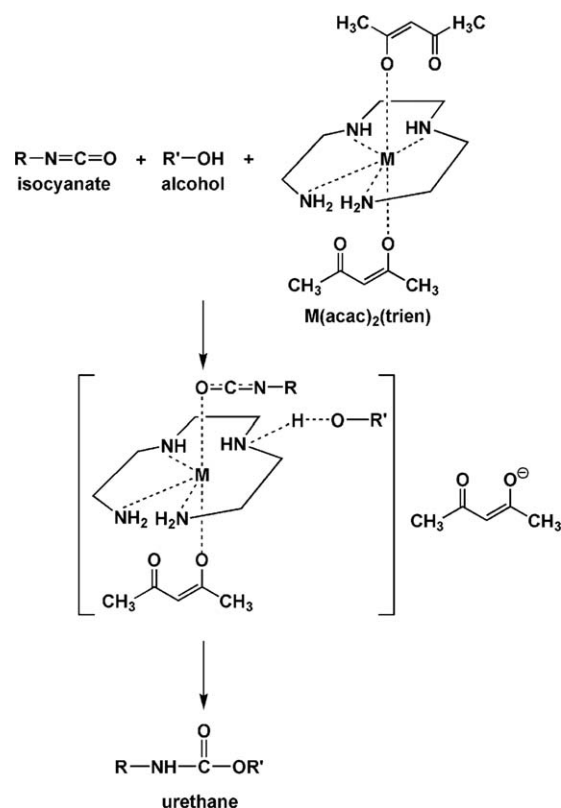
Scheme 3. Proposed catalytic mechanism of M(acac)$_2$(trien).

Figure 5. SEM micrographs of RPUR foams catalyzed by metal acetylacetonate–amine complexes in perpendicular (top view) and parallel (side view) to the foam-rising direction: (a) $Cu(acac)_2$(trien), perpendicular; (b) $Cu(acac)_2$(trien), parallel; (c) $Zn(acac)_2$(en), perpendicular; (d) $Zn(acac)_2$(en), parallel; (e) $Zn(acac)_2$(trien), perpendicular; and (f) $Zn(acac)_2$(trien), parallel.

hydroxyl groups of blowing agent (water) to give CO_2. It was found that rise time of RPUR foams agrees with their rise profiles (Figure 4). When compared with $Cu(acac)_2$(trien), DMCHA took shorter rise time to reach its full height. RPUR foam prepared from copper and zinc acetylacetonate–amine complexes showed similar trend to that of DMCHA. All copper and zinc acetylacetonate–amine complexes had lower catalytic activity in blowing reaction than DMCHA as RPUR foams catalyzed by metal complexes took longer time to reach their full height. The metal acetylacetonate–amine complexes showed longer initial time than DMCHA and exhibited a faster rise curve in the latter stage.

When tin compound was used with tertiary amine as catalyst in the preparation of polyurethane foam, the mechanism of synergistic effect between tin and amine catalysts is observed.[2] Copper and zinc acetylacetonate–amine complexes contain metal atom and amine groups in their structures. The catalytic mechanism of gelling reaction between isocyanate and hydroxyl groups is proposed as shown in Scheme 3. The metal atom (copper and zinc) and amine groups show synergistic effect in catalysis. The metal atom acts as Lewis acid and coordinates to the oxygen atom of the NCO group, which causes the NCO carbon to be more electrophilic. The nitrogen atom in metal acetylacetonate–amine complexes interacts with the proton of

hydroxyl group and causes the hydroxyl oxygen to be more nucleophilic, which then reacts with the isocyanate group to give urethane linkage. The amine unit in metal acetylacetonate–amine complex is important in catalytic process. $Zn(acac)_2(en)$ has one ethylenediamine unit, and therefore, $Zn(acac)_2(en)$ has lower catalytic activity than $Zn(acac)_2(trien)$.

For the reaction time of RPUR foam catalyzed by metal nitrate–amine complexes (Table II), $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2(trien)$, and $Cu(NO_3)_2(tetraen)$ had lower catalytic activity than metal acetylacetonate–amine complexes and DMCHA. This might be due to the steric hindrance of NO_3 group. $Cu(NO_3)_2(en)$ gave shorter reaction time when compared with $Cu(NO_3)_2(trien)$ and $Cu(NO_3)_2(tetraen)$. This is due to the steric hindrance of amine in the order tetraen > trien > en.

In comparison with our previous work,[18] the problem that $Cu(OAc)_2(en)_2$ catalyst has fast rise profile in the middle stage can be solved. All metal acetylacetonate–amine and metal nitrate–amine complexes have slower rise profile than $Cu(OAc)_2(en)_2$. RPUR foam samples having the dimension of $10.0 \times 10.0 \times 10.0$ cm^3 can be easily prepared by pouring the mixture of starting material into the mold. This is because all metal complexes have longer gel time than $Cu(OAc)_2(en)_2$.

NCO conversion of RPUR foams was determined from the peak area of NCO group at 2277 cm^{-1} in the ATR-IR spectra as shown in the following equation:[23]

$$\text{Isocyanate conversion (\%)} = [1 - (NCO^t/NCO^i)] \times 100,$$

where NCO^t is the area of isocyanate peak at time t, which is the time after the foam was kept at room temperature for 48 h to complete the polymerization reaction. NCO^i is the area of isocyanate peak at the initial time. The isocyanate peak area is normalized by the aromatic ring peak area at 1595 cm^{-1}. All metal acetylacetonate–amine complexes gave quantitative NCO conversions. The NCO conversions of RPUR foams catalyzed by metal acetylacetonate–amine and metal nitrate–amine complexes at NCO index of 100 are 98.6–99.2.

Physical and Mechanical Properties of RPUR Foams

Compressive strength of RPUR foams catalyzed by metal acetylacetonate–amine complexes in parallel and perpendicular to the foam-rising direction is shown in Table II. It was found that the compressive strength in parallel to the foam-rising direction is higher than those in perpendicular to the foam-rising direction. These data indicate that the cell structures of the foam sample are anisotropic structures as the foam cells were elongated in the foam-rising direction. The order of compressive strength of RPUR foams obtained from different catalysts are DMCHA > Zn(acac)_2(en) > Cu(acac)_2(trien) > Zn(acac)_2(trien). For metal acetylacetonate–amine complexes, compressive strength increases with increase in foam density. RPUR foams prepared from metal nitrate–amine complexes give higher foam density than those prepared from metal acetylacetonate–amine complexes and DMCHA. The compressive strength of RPUR foam catalyzed by $Cu(NO_3)_2(trien)$ is comparable with that catalyzed by DMCHA, whereas the compressive strength of RPUR foams prepared from $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(tetraen)$ is lower than that prepared from DMCHA.

SEM micrographs of RPUR foams catalyzed by $Zn(acac)_2(en)$, $Cu(acac)_2(trien)$, and $Zn(acac)_2(trien)$ (Figure 5) show that the foams have closed cell structure. Cell morphology is spherical and elongated in perpendicular (top view) and parallel (side view) to the foam-rising direction, respectively. $Zn(acac)_2(en)$, $Cu(acac)_2(trien)$, and $Zn(acac)_2(trien)$ show similar cell structure with uniform cell size. RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2(trien)$, and $Cu(NO_3)_2(tetraen)$ have high density, and therefore, they are not suitable for application as insulating materials. Their SEM micrographs show nonuniform cell structures with different cell sizes.

CONCLUSIONS

Metal acetylacetonate–amine and metal nitrate–amine complexes are synthesized using a simple procedure and used as catalysts for RPUR foam preparation. The reaction times in RPUR foam preparation are investigated, namely, cream time, gel time, tack-free time, and rise time. All metal acetylacetonate–amine and metal nitrate–amine complexes give quantitative isocyanate conversion, which indicates the completeness of polymerization reaction. In comparison with our previous work, all metal acetylacetonate–amine and metal nitrate–amine complexes have longer gel time and slower rise profile than copper acetate–ethylenediamine complex [$Cu(OAc)_2(en)_2$]. Therefore, preparation of RPUR foams in the mold can be carried out easily. RPUR foams prepared from $Cu(acac)_2(trien)$, $Zn(acac)_2(en)$, and $Zn(acac)_2(trien)$ showed good catalytic reactivity and mechanical properties. The order of catalytic reactivity is $Cu(acac)_2(trien) > Zn(acac)_2(trien) > Zn(acac)_2(en)$.

REFERENCES

1. Woods, G. In The ICI Polyurethanes Book; Woods, G.; Sparrow, D., Eds.; Wiley: The Netherlands, 1990; Chapter 7, p 127.

2. Randal, D.; Lee, S. In Huntsman Polyurethanes—The Polyurethanes Book; Randal, D.; Lee, S., Eds.; Wiley: United Kingdom, 2002; Chapter 9, p 141; Chapter 15, p 229.

3. Wagh, Y. S.; Bhanage, B. M. Tetrahedron. Lett. 2012, 53, 6500.

4. Shimomoto, H.; Hara, Y.; Itoh, T.; Ihara, E. Macromolecules 2013, 46, 5483.

5. Pastusiak, M.; Dobrzynski, P.; Kasperczyk, J.; Smola, A.; Janeczek, H. *J. Appl. Polym. Sci.* **2014**, DOI: 10.1002/app.40037.

6. Zhao, J. B.; Li, K. Y.; Yang, W. T. *J. Appl. Polym. Sci.* **2007**, *106*, 590.

7. Smith, J. D. B. *J. Appl. Polym. Sci.* **1981**, *26*, 979.

8. Kalyanam, N.; Gandhi, V. G.; Sivaram, S. *Polym. Bull.* **1984**, *11*, 105.

9. Gupta, K. C.; Sahoo, S. *J. Appl. Polym. Sci.* **2001**, *81*, 2286.

10. Inoue, S.; Nagai, Y. *Polym. J.* **2005**, *37*, 380.

11. Cakic, S. M.; Stamenkovic, J. V.; Djordjevic, D. M.; Ristic, I. S. *Polym. Degrad. Stab.* **2009**, *94*, 2015.

12. Cakic, S. M.; Nikolic, G. S.; Stamenkovic, J. V. *Polym. Plast. Technol.* **2007**, *46*, 299.

13. Sardon, H.; Irusta, L.; Fernández-Berridi, M. *J. Prog. Org. Coat.* **2009**, *66*, 291.

14. Inoue, S.; Nagai, Y.; Okamoto, H. *Polym. J.* **2002**, *34*, 298.

15. Sharma, S.; Barooah, N.; Baruah, J. B. *J. Mol. Catal. A* **2005**, *229*, 171.

16. Indra, A.; Mobina, S. M.; Bhaduri, S.; Lahiri, G. K. *Inorg. Chim. Acta* **2011**, *374*, 415.

17. Peter, G.; Aubel, P. G.; Shaista, S.; Khokhar, S. S.; Driessen, W. L.; Challa, G.; Reedijk, J. *J. Mol. Catal. A* **2001**, *175*, 27.

18. Pengjam, W.; Saengfak, B.; Ekgasit, S.; Chantarasiri, N. *J. Appl. Polym. Sci.* **2012**, *123*, 3520.

19. Niven, M. L.; Percy, G. C. *Transit. Metal. Chem.* **1978**, *3*, 267.

20. Paulovicova, A.; El-Ayaan, U.; Fukuda, Y. *Inorg. Chim. Acta* **2001**, *321*, 56.

21. Asadi, H.; Golchoubia, H.; Welter, R. *J. Mol. Struct.* **2005**, *779*, 30.

22. Horikoshi, R.; Funasako, Y.; Yajima, T.; Mochida, T.; Kobayashi, Y.; Kageyama, H. *Polyhedron* **2013**, *50*, 66.

23. Modesti, M.; Lorenzetti, A. *Eur. Polym. J.* **2001**, *37*, 949.