

# Application of Tin(IV) Porphyrin Complexes as Novel Catalysts for the Synthesis of New Copolyurethanes with Cyclopeptide Moiety

Fateme Rafiemanzelat,<sup>1</sup> Elahe Abdollahi,<sup>1</sup> Majid Moghadam,<sup>2</sup> Valiollah Mirkhani,<sup>2</sup> Shahram Tangestaninejad,<sup>2</sup> Iraj Mohammadpoor-Baltork<sup>2</sup>

<sup>1</sup>Organic Polymer Chemistry Research Laboratory, Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, I.R. Iran

<sup>2</sup>Catalysis Division, Department of Chemistry, University of Isfahan, Isfahan 81746-73441, I.R. Iran

Received 8 February 2010; accepted 28 May 2011

DOI 10.1002/app.35022

Published online 5 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** New electron deficient tin(IV) porphyrins were used as efficient catalysts for the reaction of 4,4'-methylene-bis-(4-phenylisocyanate) (MDI), with *L*-leucine anhydride cyclodipeptide (LAC) and polyethyleneglycol-400 (PEG-400) and the results were compared with those obtained in the presence of a commercial catalyst, dibutyltin dilaurate (DBTDL). Molar ratio of catalysts to MDI, polymerization reaction time, viscosity, and yield of the resulting poly(ether-urethane-urea)s (PEUU) were compared in the presence of different catalysts. The rate

of N=C=O conversion in the presence of each catalysts under the same reaction conditions was also compared and followed by FT-IR N=C=O absorption band. FT-IR, GPC, and viscosity studies have shown that tin(IV) porphyrins afford higher viscosity and reaction progress. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 638–646, 2012

**Key words:** poly(ether-urethane-urea)s; biomimetic catalysts; metalloporphyrins; DBTDL

## INTRODUCTION

Electron deficient metalloporphyrins such as Cr(tpp)Cl, Fe(tpp)OTf, Cr(tpp)OTf, and Sn(tpp)X<sub>2</sub> (X=OTf or BF<sub>4</sub>) have been used as mild Lewis acid catalysts in organic synthesis.<sup>1–10</sup> Some metalloporphyrins were also designed to mimic the function of cytochrome P-450. All of these studies led to finding a number of synthetically useful catalysts for the selective oxidation of hydrocarbons and different synthetic applications.<sup>11–21</sup>

Tin complexes were extensively studied for a variety of applications. Different tin catalysts have been developed for different organic and polymerization reactions.<sup>22–28</sup> Tin(IV) porphyrins have attracted attention in recent years due to the successful utilization of their particular properties granted by the highly charged metal center.<sup>29,30</sup> Tin(IV) porphyrins have been also investigated for applications in catalysis,<sup>31</sup> biomedicine,<sup>32</sup> and synthesis of nano materi-

als.<sup>33,34</sup> Sn<sup>IV</sup>(tpp)(BF<sub>4</sub>)<sub>2</sub> and Sn<sup>IV</sup>(tpp)(OTf)<sub>2</sub> have been used in the alcoholysis, hydrolysis, acetolysis reactions. They also have been used for the conversion of epoxides to thiiranes with ammonium thiocyanate and thiourea, for the preparation of 1,3-dioxolanes from epoxides, for methoxymethylation of alcohols and phenols and for selective acetylation of alcohols and phenols with acetic anhydride at room temperature (RT).<sup>35–37</sup> Although metalloporphyrins are widely used in different organic transformations, there have been few studies on their catalytic activity as Lewis acids.<sup>8–10,14–20,35–37</sup> Because the tin(IV)-porphyrins are mild Lewis acids, we decided to explore their ability in the reaction of amine or hydroxyl groups with isocyanate compounds. To the best of our knowledge tin(IV) porphyrins have not been used for the preparation of polyurethanes or polyureas.

A large number of degradable polymers have been used in biomedical applications, or as environmental friendly polymers. Degradable polymers are generally achieved by incorporating labile moieties susceptible to degradation into the polymer chain.<sup>38,39</sup> Some important classes of degradable polymers are poly( $\alpha$ -hydroxy acid)s, poly( $\alpha$ -amino acid)s, synthetic peptide-based polymers and their different block copolymers. Amino acid anhydrides, which are prepared from amino acids, are important precursors and may be good candidates for the

Correspondence to: F. Rafiemanzelat (F.rafiamanzelat@chem.ui.ac.ir or F.rafiamanzelat@yahoo.com).

Contract grant sponsor: Iran National Science Foundation (INSF); contract grant number: 86121108.

Contract grant sponsor: Research Affairs Division University of Isfahan.

preparation of degradable polymers.<sup>40</sup> On the other hand, amino acid anhydrides such as 2,5-diketopiperazines have attracted much attention due to their biological properties such as the inhibition of plasminogen activator inhibitor-1 (PAI-1) and alteration of cardiovascular and blood-clotting functions. They have also activities as anti-tumour, antiviral, antifungal, and antibacterial.<sup>41,42</sup>

The successful applications of tin(IV) porphyrins as mild Lewis acids in selective acetylation of alcohols and phenols encouraged us to investigate the potential of these complexes for the reaction of N—H and O—H groups with N=C=O group to afford the corresponding carbamate esters and urea groups for the formation of new co-polyurethanes (PU). In our previous work, LAC was synthesized via a green method, under microwave irradiation, as well as conventional heating method. Then polymerization reaction of MDI, PEG, and LAC in the presence of triethyl amine, pyridine, and DBTDL as well as hydrolytic degradation of the resulting PEUUs were studied.<sup>43</sup> In the present work, for the first time, we report the application of tin(IV) porphyrin catalysts for the synthesis of novel degradable PU copolymers, based on PEG and an amino acid anhydride. The optimized reaction conditions obtained in our previous work were used here to study and compare the effect of different catalysts on the polymerization reaction of MDI, LAC, and PEG.

## EXPERIMENTAL

### Materials

MDI (Aldrich, 98%) was used without further purification. PEG-400 was purchased from Merck and dried under vacuum at 80°C for 8 h. The 1-methyl-2-pyrrolidone (NMP) (Merck, 99.5%) were distilled under reduced pressure over BaO (Aldrich, 97%). DBTDL (Merck, 97%), and (S)-(+)-Leucine (Merck, 99%) were used as received. Ethylene glycol (EG) (Merck, 99%) was distilled under reduced pressure over CaO (Merck, 97%).

### Instruments and measurements

Proton nuclear magnetic resonance, <sup>1</sup>H NMR, (400 MHz) spectra were recorded on a Bruker, Avance 400 instrument in dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) at RT. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), multiplet (m), and broad (br). FT-IR spectra were recorded on a Jasco FT-IR spectrophotometer. Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies are reported in wave number (cm<sup>-1</sup>). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s),

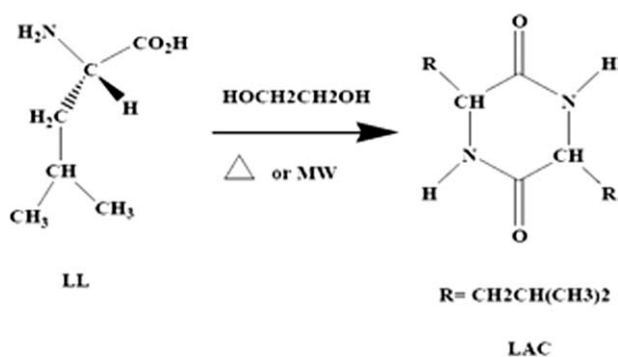
and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler-Toledo TG-50 Thermal Analyzer under N<sub>2</sub> atmosphere at heating rate of 20°C min<sup>-1</sup>. The initial and peak temperatures were read at the beginning and in the middle of the decomposition step obtained by TGA curve. The weight average molecular weight (*M*<sub>w</sub>) and polydispersity index (PDI) of the polymer samples were determined using a gel permeation chromatography system (GPC), WATERS-150-C. Calibration and measurements were made at a flow rate of 1 mL min<sup>-1</sup>, in DMF at 35°C as eluent. Monodispersed poly(ethylene glycol) standards were used to obtain a calibration curve.

### Preparation of tin(IV) (tpp) catalysts

Sn<sup>IV</sup>(tpp)(OTf)<sub>2</sub> (TPO) and Sn<sup>IV</sup>(Br<sub>8</sub>tpp)(OTf)<sub>2</sub> (TPO-Br) were prepared according to the reported procedure by the reaction of Sn<sup>IV</sup>(tpp)Cl<sub>2</sub> and Sn<sup>IV</sup>(Br<sub>8</sub>tpp)Cl<sub>2</sub> with AgCF<sub>3</sub>SO<sub>3</sub>.<sup>17,31,36,37</sup> Tetraphenylporphyrin (tpp) was prepared, brominated and metalated according to the literature.<sup>44-47</sup>

### Synthesis of PEUUs block copolymers in the presence of Sn catalysts

A typical preparation of PEUUs by pre-polymerization method, according to previously obtained optimized reaction conditions, is as following: in a 25-mL two-necked round bottom flask, equipped with drying tube and N<sub>2</sub> balloon, LAC (0.055 g, 2.43 × 10<sup>-4</sup> mol) was dissolved in NMP 1% (0.15 mL) (NMP containing 1% w/w LiCl as solubility assistant) at 120°C, then MDI (0.122 g, 4.87 × 10<sup>-4</sup> mol) was added and the mixture was heated at 120°C for 15 min. After that, the reaction mixture was cooled to 80°C, and the catalyst (TPO, TPO-Br, or DBTDL) in NMP 1% was added. The reaction mixture was stirred at 90°C for 2 h and at 100°C for 2 h. During this period, appropriate amounts of NMP 1% were added upon increasing the viscosity of the reaction mixture. Then, it was cooled to 50°C, and a solution of PEG-400 (0.097 g, 2.43 × 10<sup>-4</sup> mol) in 0.2 mL of NMP 1% was added. The temperature was gradually increased up to 90°C during 1 h. The reaction mixture was stirred at 90°C for 1 h and then heated up to 110°C over a period of 3 h and NMP 1% was added as required. The total solid content of the reaction mixture was kept at 40% W/V. Then the viscous solution of reaction mixture was poured into 15 mL of water. After vigorous grinding and stirring in water, the precipitated polymer was isolated. Additional purification was applied by re-dissolving and re-precipitation of polymer in DMF (or DMF



**Scheme 1** Preparation of *L*-leucine anhydride cyclodipeptide (LAC).

1%, DMF containing 1% w/w LiCl) and water, respectively. The precipitated polymer was collected by filtration, washed thoroughly with ethanol,  $\text{CH}_2\text{Cl}_2$ , THF, and water, successively, and dried at  $80^\circ\text{C}$  for 6 h under vacuum. The FT-IR and  $^1\text{H}$  NMR spectra were consistent with the assigned structure:

FT-IR peaks ( $\text{cm}^{-1}$ , KBr): 3320 (m, br) NH st., 3196 (m, br) NH st., 3099 (m) NH st., 3056 (m) CH aromatic st., 2956 (m) CH st., 2926 (m) CH st., 2870 (m) CH st., 1772 (s, sh) C=O urethane st., 1674 (s) C=O urea st., 1596 (m) C=C st., 1540 (m) C-N st. + NH bend, 1509 (s) C=C st., 1456 (m) C=C st., 1412 (m) C-N st., 1408 (m) CH bend, 1385 (m), 1368 (w), 1347 (w), 1313 (m), 1250 (m) C-N st. + NH bend, 1233 (m), 1201 (w), 1179 (w), 1142 (w), 1119 (m) C-O-C ether st, 1042 (m) O=C-O-C st., 1018 (w), 917 (w), 813 (w) NH bend, 764 (w) O=C-O, 663 (w), 509 (w), 482 (w).  $^1\text{H}$  NMR peaks,  $\delta$  ppm: 0.90–0.95 (distorted d,  $\text{CH}_3$ , side chain of LAC), 1.4–1.6 (m, diastereotopic hydrogens of  $\text{CH}_2$ , side chain of LAC), 1.8–1.9 (m, CH, side chain of LAC), 3.2–3.4 (m,  $\text{CH}_2$  of PEG), 3.6–3.8 (m,  $\text{CH}_2$  of PEG), 3.8–4.2 (m,  $\text{CH}_2$  of MDI moiety and  $\text{CH}_2$  of urethane link-

ages), 4.4–4.6 (m, CH of LAC cycle), 7.1–7.4 (br, d, Aromatic CH), 8.1–8.6 (br, NH urea, urethane).

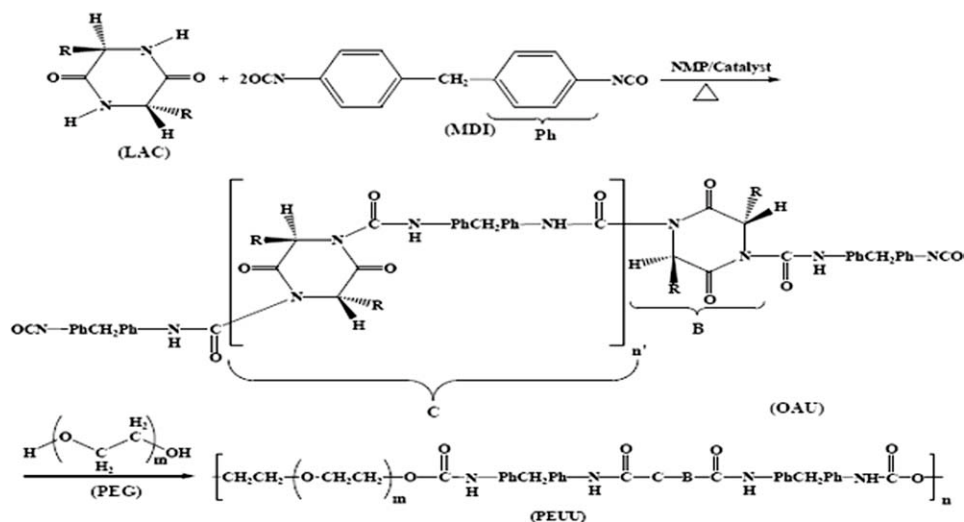
The above mentioned polymerization method was repeated in the presence of different catalysts [(TPO), (TPO-Br), or DBTDL] and/or different molar ratio of each catalyst to MDI.

## RESULTS AND DISCUSSION

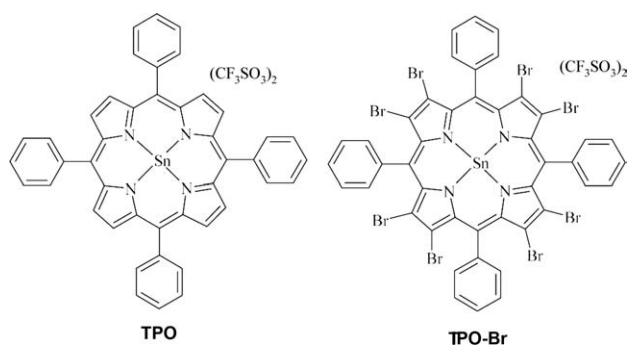
### Monomer and polymer synthesis

LAC, which is an amino acid based monomer, was prepared via heating of *L*-leucine (LL) in dried EG and recrystallized from hot ethanol (Scheme 1).<sup>43,48</sup> The applicability of microwave irradiation for the preparation of LAC was also studied in our previous work.<sup>43</sup> The chemical structure and purity of the resulting compound were confirmed by FT-IR,  $^1\text{H}$  NMR, melting point measurement, and thin layer chromatography (TLC).

The PEUU multiblock copolymers were synthesized according to Scheme 2 by a two-steps method. LAC, as a preformed amide containing heterocyclic monomer, was reacted with MDI diisocyanate to afford N=C=O terminated hard segment containing urea linkage which was used as NCO-terminated oligo amide-urea (OAU). Reaction of the resulting OAU pre-polymer with PEG-400 was the second step to furnish new PEUUs. The effect of polymerization conditions such as reaction time and temperature, reaction media (solvent), and soft segment length on the viscosity and yield of the resulting PEUUs have been studied in our previous work and the optimized reaction condition was obtained and used here.<sup>43</sup> In this work, the effect of tin(IV) complexes on the reaction of N-H (Step 1) or O-H (Step 2) groups with N=C=O functional group for producing the corresponding urea or urethane



**Scheme 2** Preparation of PEUUs by two step polymerization reaction of MDI, LAC, and PEG-400.



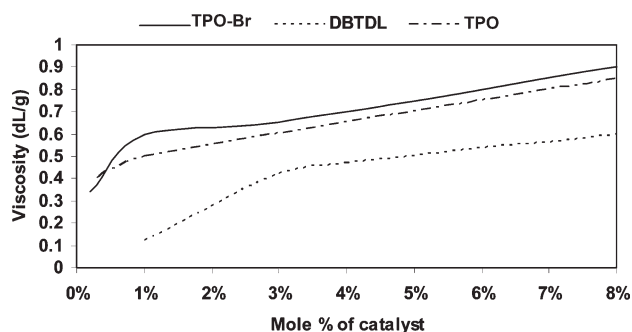
**Figure 1** Structure of Sn(tpp)(OTf)<sub>2</sub> (TPO) and Sn(Br<sub>8</sub>tpp)(OTf)<sub>2</sub> (TPO-Br) catalysts.

linkages was studied. The effect of Sn catalysts on the synthesis of novel PU copolymers containing cyclopeptide segments was compared.

### Catalyst effect

The copolymerization reaction was performed in the presence of different catalysts such as TPO, TPO-Br (Fig. 1), or DBTDL and different molar ratio of each catalyst to MDI.

It was found that by increasing the molar ratio of each catalyst to MDI (M%), the viscosities of the resulting polymers increased, but after utmost 3 M%, there was not observed much drastic changes in resulting viscosities (Fig. 2). At 8 M%, the viscosities of the resulting polymers are 0.8, 0.9, and 0.6 (dL g<sup>-1</sup>) in the presence of TPO, TPO-Br, or DBTDL, respectively. At 3 M%, the resulting viscosities are 0.6, 0.65, and 0.42 (dL g<sup>-1</sup>), and at 1 M% they are 0.5, 0.6, and 0.12 dL g<sup>-1</sup>, respectively. It can be seen that Sn(IV) porphyrin catalysts afforded polymers with higher viscosities than that of DBTDL. At 1 M%, the yields of resulting PEUUs are 69, 72, and 75% in the presence of TPO, TPO-Br, or DBTDL, respectively. At 3 M%, the resulting yields are 72,



**Figure 2** Variations of viscosities of PEUUs with respect to the mole ratio of each catalyst to MDI (M%). Polymerization reactions were proceeded for 10 h under the same reaction conditions mentioned in Synthesis of PEUUs Block Copolymers in the Presence of Sn Catalysts section.

**TABLE I**  
Comparing the Decay of NCO Group by Monitoring FTIR Peak Intensity% at 2260 cm<sup>-1</sup> at Different Reaction Time After Addition of Each Catalyst to the Reaction Mixture

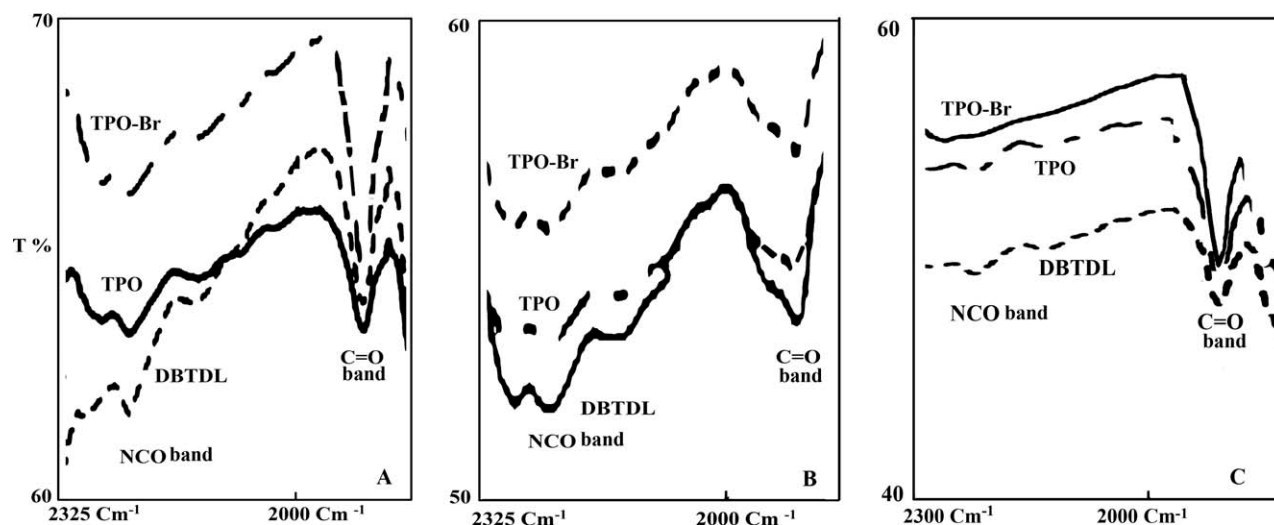
Reaction time (h)/reaction catalyst	DBTDL	TPO	TPO-Br
1	49.25 <sup>a</sup>	59.50 <sup>a</sup>	67.44 <sup>a</sup>
2	50.81 <sup>a</sup>	61.11 <sup>a</sup>	67.67 <sup>a</sup>
3	55.73 <sup>a</sup>	64.19 <sup>a</sup>	67.81 <sup>a</sup>
4	61.53 <sup>a</sup>	64.59 <sup>a</sup>	67.9 <sup>a</sup>
5	62.56 <sup>a</sup>	67.66 <sup>a</sup>	75.47 <sup>a</sup>
6	67.66 <sup>a</sup>	70.58 <sup>a</sup>	76.02 <sup>a</sup>
7	70.21 <sup>a</sup>	72.27 <sup>a</sup>	77.61 <sup>a</sup>

<sup>a</sup> FTIR peak intensity% of NCO group.

76, and 76%, and at 8 M% they are 75, 80, and 78%, respectively. However; the observed trend in resulting yields can be doubtful and not reproducible. It may be due to the fact that the resulting polymer product may be lost during successive washing and purification process. It can be said that economic amounts of each catalysts for preparation of these kinds of PU co-polymers are below 3 M%. It can be inferred that TPO-Br is a superior catalyst, because with less amount of catalyst consumption the resulting polymer had higher viscosity and yield than those of polymers resulted in the presence of other catalysts. It can be seen that its economic consumption is below 2 M% (Fig. 2).

The rate of N=C=O conversion in the presence of different catalysts was compared and followed by N=C=O absorption band at 2260 cm<sup>-1</sup>, at the same molar ratio of each catalyst to MDI (1 M%), and under the same reaction conditions (Table I). After addition of catalyst to the reaction mixture, exact amount of the viscous solution was taken out at every 15-min intervals and cast on a preformed KBr pellets for film forming. In the FT-IR analysis, integrated intensities of the absorption bands were corrected for sample thickness differences using the CH<sub>2</sub> stretching band near 2956 cm<sup>-1</sup> as a normalizing factor. Figure 3 illustrates the FT-IR spectra of N=C=O bands of reaction mixtures in the presence of different catalysts, after 1, 4, and 7 h, respectively. It can be seen that the intensity of peaks corresponding to unreacted N=C=O during different steps of the reaction has the following order: DBTDL > TPO > TPO-Br. Figure 4 compares FT-IR peak intensities of the N=C=O bands of reaction mixtures catalyzed by different catalysts at different reaction times during Step 1 (pre-polymerization, formation of urea linkage by the reaction of LAC with MDI) and Step 2 (formation of urethane linkage by the reaction of PEG with NCO-terminated OAU) of the polymerization reaction. The same conclusion can be made, i.e., during all periods of the polymerization, including

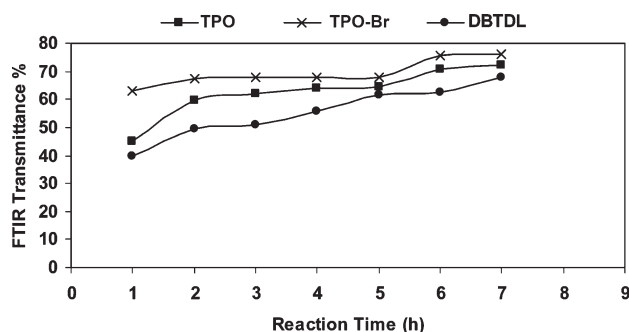




**Figure 3** FTIR spectra of different reaction mixtures containing DBTDL, TPO, or TPO-Br. Comparing the decay of NCO peak at different reaction time of about 1 h (A), 4 h (B), and 7 h (C) after addition of each catalyst to the reaction mixture. The spectra were moved up for better comparison of the ratio of peak area or peak intensities. Spectra A concern Step 1 of polymerization reaction, reaction of NCO and NH groups of LAC. Spectra B are related to the starting of Step 2 of copolymerization reaction by adding PEG.

urea formation and urethane formation, the reaction progress in the presence of different catalysts, is in the following order: TPO-Br > TPO > DBTDL.

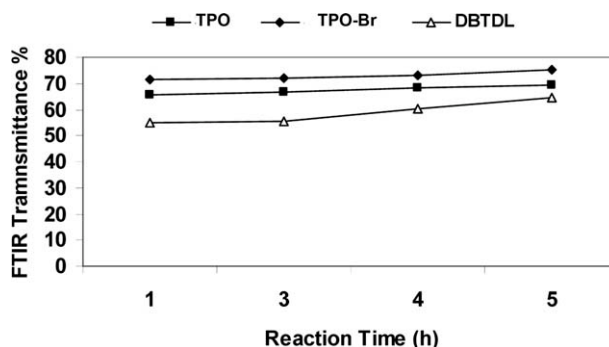
To shed some more light on this issue, that where the above mentioned catalytic activity order will preferentially happen, during Step 1 or Step 2 of copolymerization reaction, two separate homo-polymerization reaction of MDI/LAC or MDI/PEG was studied in the presence of different catalysts at the same molar ratio of each catalyst to MDI (1 M%), and under the same reaction conditions. The rate of  $\text{N}=\text{C}=\text{O}$  conversion was compared and followed by  $\text{N}=\text{C}=\text{O}$  absorption band at  $2260\text{ cm}^{-1}$ . FT-IR peak intensities of the  $\text{N}=\text{C}=\text{O}$  bands of reaction mixtures catalyzed by different catalysts as a function of reaction time were measured (Figs. 5 and 6). Figure 5 shows FTIR monitoring of NCO conversion in the presence of different catalysts at 1 M%, during



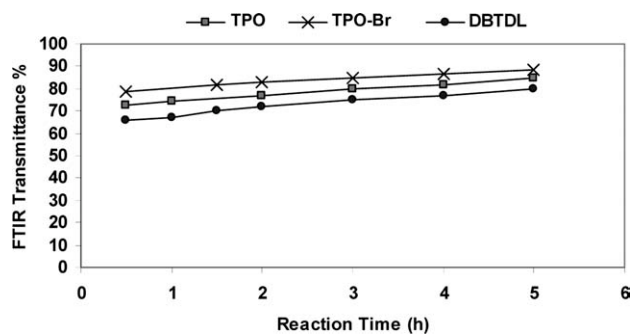
**Figure 4** FTIR monitoring of NCO conversion of different reaction mixtures in the presence of different catalysts under the same reaction conditions which was obtained on the basis of NCO peak intensity vs. reaction time during Steps 1 and 2 of polymerization reaction.

polymerization reaction of MDI with LAC, Poly(urea) formation reaction. The molar ratio of MDI to LAC was 1. Figure 6 shows the same study for polymerization reaction of MDI with PEG, poly(urethane) formation reaction. According to the results presented in Figures 5 and 6, it can be seen that above catalysts affected both steps of co-polymerization reactions including urea and urethane formation reactions, in the order of TPO-Br > TPO > DBTDL.

During co-polymerization reaction, LAC was reacted with MDI in the first step and the ratio of MDI/LAC was 2. Then PEG was added after 5 h to the above mentioned reaction mixture, which is expected that it contains NCO-terminated OAU. Thus the ratio of NCO/OH in the reaction mixture was 1. It is assumed that in the second step PEG diol reacts with NCO-terminated OAU to form

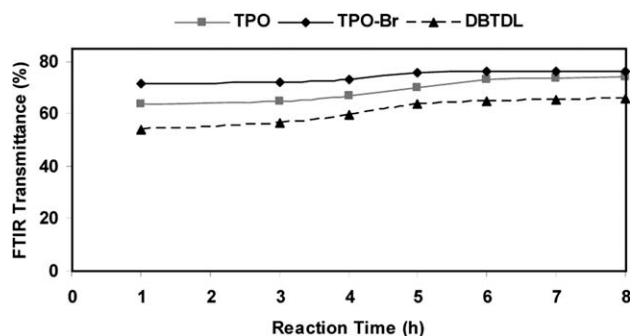


**Figure 5** FTIR monitoring of NCO conversion of different reaction mixtures containing different catalysts at 1 M%, under the same reaction conditions which was obtained on the basis of NCO peak intensity vs. reaction time during polymerization reaction of MDI with LAC, Poly(urea) formation reaction. Molar ratio of MDI/LAC was 1.

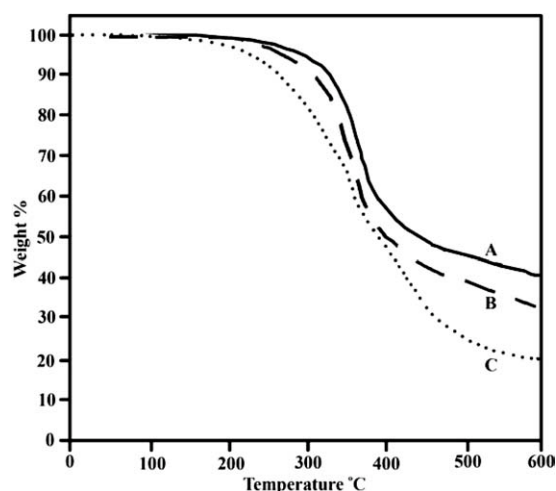


**Figure 6** FTIR monitoring of NCO conversion of different reaction mixtures containing different catalysts at 1 M%, under the same reaction conditions which was obtained on the basis of NCO peak intensity vs. reaction time during polymerization reaction of MDI with PEG, poly (urethane) formation reaction. Molar ratio of MDI/PEG was 1.

urethane linkages resulted in final co-polymer, PEUUs. To confirm this assumption, we conducted another study by following NCO consumption with respect to reaction time via monitoring FT-IR peak intensities of the  $N=C=O$  bands of reaction mixtures containing MDI/LAC catalyzed by different catalysts (Fig. 7). The molar ratio of MDI/LAC in this study was 2 and reaction was followed for 8 h without addition of PEG. It can be seen that after almost 5 h of reaction progress, peak intensities of the  $N=C=O$  bands reached constant value. It can be inferred that after these period of reaction time all LAC monomers were consumed and reacted with MDI, resulting NCO-terminated OAUs or LAC concentration in the reaction mixture is too low to be able to affect reaction progress. Thus it can be said that during Step 2 of co-polymerization reaction after addition of PEG to the above reaction mixture there is not much competition between NH of LAC and OH of PEG to react with NCO functional group.



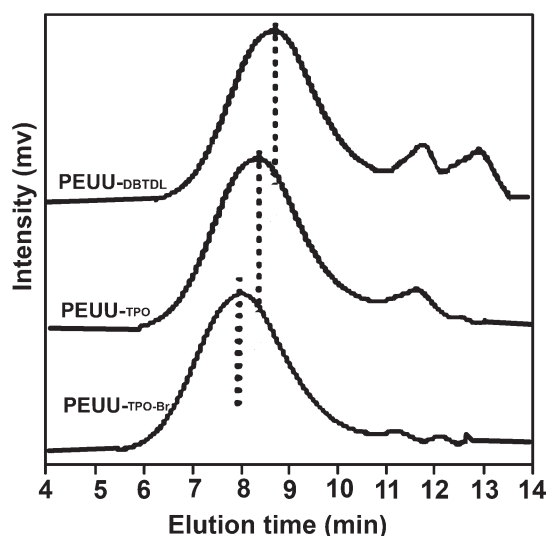
**Figure 7** FTIR monitoring of NCO conversion of different reaction mixtures containing different catalysts at 1 M%, under the same reaction conditions which was obtained on the basis of NCO peak intensity vs. reaction time during polymerization reaction of MDI with LAC, NCO-terminated oligo amide-urea formation reaction. Molar ratio of MDI/LAC was 2.



**Figure 8** TGA thermograms of different PEUUs samples prepared in the presence of different catalysts at 1 M% after 7 h of the polymerization reaction. A: TPO-Br, B: TPO, C: DBTDL.

Therefore reaction of PEG with MDI or NCO-terminated OAU is the dominate reaction. Another conclusion obtained up on Figure 7 is that, NH of urea linkages presented in OAU can not compete with PEG because no much consumption of NCO peak can be observed during 4–8 h of reaction time and NCO band intensity stays constant. Thus there is no serious competition between urea NH of OAU and OH of PEG during Step 2 as well. The same conclusion up on the results presented in Figures 5 and 6 can be achieved and it can be said that above catalysts affected polymerization reactions during both Step 1 and 2, in the order of TPO-Br > TPO > DBTDL. This reactivity order can be confirmed by another feature of Figure 7. It can be seen that intensity of NCO peaks of reaction mixtures containing different catalysts reached a constant value in the order of TPO-Br > TPO > DBTDL, after 4, 5, and 6 h in the presence of TPO-Br, TPO, and DBTDL, respectively. It means that after the same reaction time, different reaction mixtures containing different catalysts have different reaction progress. This conclusion was confirmed by TGA and GPC studies.

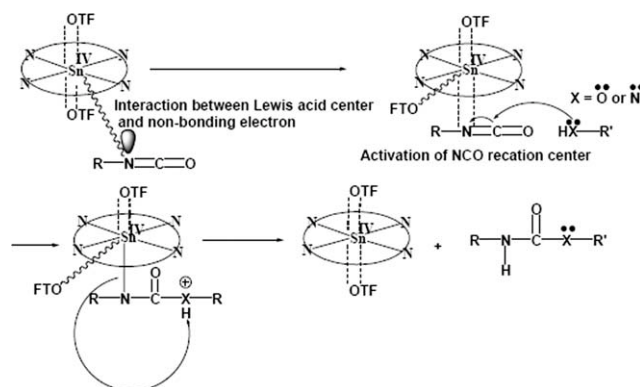
The TGA curves of PEUUs prepared in the presence of different catalysts are shown in Figure 8. It can be seen that PEUU prepared in the presence of TPO-Br shows slightly higher thermal stability compared to other systems. Enhancement of thermal stability could be attributed to the better reaction completion of this sample during Step 1 (pre-polymerization) as well as Step 2 (chain extension) (Figs. 4–7). It means that in this case incorporation of thermally stable hard segments during Step 1 and polymer molecular weight (Fig. 9) are higher than those of other systems because of better reaction completion. For DBTDL catalyzed system at the given reaction time (7 h), the initial



**Figure 9** GPC elution trace for different PEUUs samples prepared in the presence of different catalysts under the same reaction conditions after 7 h. PEUU-DBTDL ( $M_w = 4.8 \times 10^4$ ,  $M_w/M_n = 3.08$ ), PEUU-TPO ( $M_w = 8.7 \times 10^4$ ,  $M_w/M_n = 2.84$ ), PEUU-TPO-Br ( $M_w = 9 \times 10^4$ ,  $M_w/M_n = 2.61$ ).

decomposition temperature and peak temperature are 150 and 350°C, respectively. While, the initial decomposition and peak temperatures are 200 and 370°C for TPO, and 223 and 376°C for TPO-Br, respectively. The thermal stability of the polymers, catalyzed with porphyrin catalysts, differ slightly in the order of TPO-Br > TPO. The percentage of weight residues at 600°C for TPO-Br, TPO, and DBTDL are 40, 32, and 20%, respectively. It implies the difference in the order of hard segments incorporation during Step 1. Thus, the overall observed thermal stabilities of different catalyzed systems differ in the order of TPO-Br > TPO > DBTDL, reflecting the difference in the order of reaction progress (polymer chain growth) and incorporation of thermally stable hard segments, which is in accordance with FT-IR results (Figs. 4–7).

The weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) of polymer samples were determined by GPC analysis. A typical GPC chromatograph of PEUUs prepared in the presence of different catalysts at the same molar ratio of each catalyst to MDI (1 M%), and under the same reaction

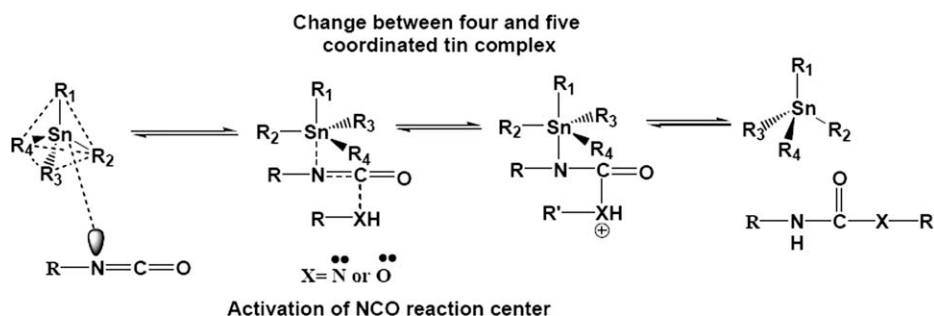


**Scheme 3** A proposed activation mechanism for interaction of tin(IV) porphyrin catalysts with reacting functional groups.

conditions after the same reaction time (7 h) are shown in Figure 9. It can be seen that PEUU prepared in the presence of TPO-Br, PEUU-TPO-Br, shows a relatively uni-modal peak in GPC chromatograph corresponding to  $M_w$  of about  $8.98 \times 10^4$ . Figure 9 also compares the GPC profiles of PEUUs prepared in the presence of TPO, PEUU-TPO, and DBTDL, PEUU-DBTDL. The later GPC profiles show a relatively di-modal profile comprising of at least two/three different components corresponding to  $M_w$  ranging from  $0.31 \times 10^4$  to  $8.71 \times 10^4$ . It can be inferred from the multi-modal GPC profiles, that these PEUUs include polymer chains with lower chain growth. PEUU-DBTDL as shown in Figure 9 exhibits shift of elution time to low molecular weight side as compared with PEUU-TPO-Br and PEUU-TPO samples. It can be concluded that during the given reaction time polymer chains growth in the presence of DBTDL was lower than those in the presence of TPO-Br and TPO. Thus the order of reaction progress obtained by FTIR study, TPO-Br > TPO > DBTDL, is confirmed by GPC results.

### Proposed mechanism

There are many articles which have studied or referred to catalytic behavior of different tin(IV) catalysts including DBTDL and tin porphyrins during



**Scheme 4** A proposed activation mechanism for interaction of DBTDL catalyst with reacting functional groups.

different reactions as well as urethane or urea formation reaction which involve the coordination of a reaction center containing lone-paired electrons of reacting species with tin center and show the existence of different possible tin hybridizations and complex geometries.<sup>11,12,49–51</sup> These results are consistent with a mechanism which involves the coordination of lone-paired electrons of nitrogen atom (N-coordination) of isocyanate group (N=C=O) with a tin complex which plays a role as a Lewis acid center (Schemes 3 and 4). It can be seen that the N-coordination of the isocyanate with a tin complex activates N=C=O reaction center for nucleophilic attack of OH or NH groups. It has been also showed that a four-coordinated tin complex changes its hybridization states (Scheme 4).

It can be inferred from schemes 3 and 4 that porphyrin ring, bromine atoms, and OTF groups because of their electron withdrawing nature can provide tin atom with a higher Lewis acid character. This, in turn creates a highly activated tin(IV) complex. Therefore tin(IV) porphyrin catalysts can activate NCO reaction center more in comparison with DBTDL. Increasing molar ratio of each catalyst to NCO provides more available sites for NCO-Sn interaction. However, a highly activated tin(IV) catalyst exchanges between its free state and NCO-Sn interacting state faster than a non-activated tin(IV) catalyst or DBTDL. Thus it can be concluded that a highly activated tin(IV) porphyrin affords less amount of catalyst than what can be achieved with DBTDL and provides PEUUs with higher chain growth at identical reaction time in comparison with DBTDL. On the other hands on account of steric hindrance of interacting groups, tin(IV) porphyrin catalysts provide a suitable geometry because of planar porphyrin ring which facilitates NCO approach to Sn. In addition DBTDL has to exchange between different hybridization state and complex geometry during its catalytic cycle (Scheme 4).

## CONCLUSION

In this study, the effect of Sn catalysts on the synthesis of novel PU copolymers containing eco-friendly segments, based on PEG and amino acid anhydride was studied. It was found that tin(IV) porphyrin catalysts are superior catalysts in comparison with DBTDL, concerning higher reaction progress, higher viscosity, and good yield of the resulting polymers at the same reaction time and catalyst consumption. Other advantages of tin(IV) porphyrin catalysts are: (1) lower tin content; relative to unit mass of DBTDL, (2) higher activity; because of electron withdrawing nature of porphyrin ring, OTF and bromine atoms which consequently renders tin atom to have a high Lewis acid character. This in turn, provides a

highly activated tin(IV) complex which affords lesser amount of effective loadings of catalysts than what can be achieved with organometallics, DBTDL. It is also possible to make analogous tin(IV) porphyrin structures with different ligands containing different substituents which enables matching of the catalyst to polyurethane formulations of different polarity and activity.

The authors extend their thanks to Prof. Shadpour Mallakpour, Miss. Zahra Rafiee and Zeynab Sori for useful help.

## References

1. Suda, K.; Sashima, M.; Izutsu, M.; Hino, F. *J Chem Soc Chem Commun* 1994, 949. (one page)
2. Takanami, T.; Hirabe, R.; Ueno, M.; Hino, F.; Suda, K. *Chem Lett* 1996, 12, 1031.
3. Firouzabadi, H.; Sardarian, A. R.; Khayat, Z.; Karimi, B.; Tangestaninejad, S. *Synth Commun* 1997, 27, 2709.
4. Firouzabadi, H.; Khayat, Z.; Sardarian, A. R.; Tangestaninejad, S. *Iran J Chem Chem Eng* 1996, 15, 54.
5. Tangestaninejad, S.; Mirkhani, V. *Synth Commun* 1999, 29, 2079.
6. Tangestaninejad, S.; Mirkhani, V. *J Chem Res (S)* 1999, 6, 370.
7. Takanami, T.; Hayashi, M.; Iso, K.; Nakamoto, H.; Suda, K. *Tetrahedron* 2006, 62, 9467.
8. Takanami, T.; Hayashi, M.; Suda, K. *Tetrahedron Lett* 2005, 46, 2893.
9. Suda, K.; Baba, K.; Nakajima, S. I.; Takanami, T. *Chem Commun* 2002, 2570.
10. Suda, K.; Kikkawa, T.; Nakajima, S.; Takanami, T. *J Am Chem Soc* 2004, 126, 9554.
11. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Taghavi, S. A. *Catal Comm* 2007, 8, 2087.
12. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Taghavi, S. A. *J Mol Catal A Chem* 2007, 274, 217.
13. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Abbasi-Larki, A. A. *Appl Catal A Gen* 2008, 349, 177.
14. Takanami, T.; Suda, K. *J Syn Org Chem Jpn* 2009, 67, 595.
15. Suda, K.; Nakajima, S. I.; Satoh, Y.; Takanami, T. *Chem Commun* 2009, 1255.
16. Takanami, T.; Nakajima, S. I.; Nakadai, S.; Hino, F.; Suda, K. *Heterocycles* 2009, 77, 365.
17. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Khajehzadeh, M.; Kosari, F.; Mehdi Araghi, M. *Polyhedron* 2010, 29, 238.
18. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Gharaati, S. *J Mol Catal A Chem* 2011, 337, 95.
19. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Gharaati, S. *Appl Organometal Chem* 2009, 23, 446.
20. Simonneaux, G.; Le Maux, P.; Ferrand, Y.; Berthelot, J. R. *Coord Chem Rev* 2006, 250, 2212.
21. Chatterjee, C.; Malcolm, H.; Chisholm, M. H. *Inorg. Chem* 2011, in press dx.doi.org/10.1021/ic200142f |
22. Graf, A.; Vuorinen, S.; Repo, T.; Kemell, M.; Nieger, M.; Markku Leskel, M. *Eur Polym J* 2008, 44, 3797.
23. Zhou, W. M.; Tomita, I. *J Inorg Organomet Polym* 2009, 19, 113.
24. De Oliveira, A. B.; Jorge, I. F.; Suarez, P. A. Z.; Basso, N. R.; De, S.; Einloft, S. *Polym Bull* 2000, 45, 341.
25. Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Polym Bull* 1991, 26, 71.



26. Kolyakina, E. V.; Vaganova, L. B.; Lado, A. V.; Piskunov, A. V.; Cherkasov, V. K.; Grishi, D. F. *Russ Chem Bull Int Ed* 2007, 56, 1363.
27. Lochee, Y.; Jhurry, D.; Luximon, A. B.; Kalangos, A. *Polym Int* 2010, 59, 1310.
28. Vaganova, L. B.; Kolyakina, E. V.; Lado, A. V.; Piskunov, A. V.; Cherkasov, V. K.; Grishin, D. F. *Polym Sci Ser A* 2008, 50, 153.
29. Arnold, D. P.; Blok, J. *Coord Chem Rev* 2004, 33, 299.
30. Kim, J. H.; Jeon, W. S.; Lim, J. H.; Hong, C. S.; Kim, J. H. *Polyhedron* 2007, 26, 2517.
31. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Shaibani, R. *Tetrahedron* 2004, 60, 6105.
32. Philippova, T. O.; Galkin, B. N.; Golovenko, N. Y.; Zhilina, Z. I.; Vodzinskii, S. V. *J Porphyrins Phthalocyan* 2000, 4, 243.
33. Song, Y.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H.; Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnut, J. A. *J Am Chem Soc* 2004, 126, 635.
34. Wang, Z.; Song, Y.; Medforth, C. J.; Shelnut, J. A. *J Am Chem Soc* 2006, 128, 9284.
35. Tangestaninejad, S.; Habibi, M. H.; Mirkhani, V.; Moghadam, M. *Synth Commun* 2002, 32, 1337.
36. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Shaibani, R. *J Mol Catal A Chem* 2004, 219, 73.
37. Gharaati, S.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Kosari, F. *Inorg Chim Acta* 2010, 363, 1995.
38. Okada, M. *Prog Polym Sci* 2002, 27, 87.
39. Hashimoto, T.; Umehara, A.; Urushisaki, M.; Kodaira, T. *J Polym Sci A Polym Chem* 2004, 42, 2766.
40. Nakano, K.; Sumitomo, Y.; Kondo, K. *Macromolecules* 1997, 30, 852.
41. Einholm, A. P.; Pedersen, K. E.; Wind, T.; Kulig, P.; Overgaard, M. T.; Jensen, J. K.; Bodker, J. S.; Christensen, A. *Biochem J* 2003, 373, 723.
42. Martins, M. B.; Carvalho, I. *Tetrahedron* 2007, 63, 9923.
43. Rafiemanzelat, F.; Abdollahi, E. *Polym Degrad Stab* 2010, 95, 901.
44. Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J Org Chem* 1987, 52, 827.
45. Adler, A. D.; Long, F. R.; Finarelli, J. D.; Gldmacher, J.; Assour, J.; Korsakoff, L. *J Org Chem* 1967, 32, 476.
46. Adler, A. D.; Long, F. R.; Kampas, F.; Kim, J. *J Inorg Nucl Chem* 1970, 32, 2443.
47. Bhyrappa, P.; Krishnam, V. *Inorg Chem* 1991, 30, 239.
48. Kunisaki, T.; Kawai, K.; Hirohata, K.; Minami, K.; Kondo, K. *J Polym Sci A Polym Chem* 2001, 39, 927.
49. Houghton, R. P.; Mulvaney, A. W. *J Org Metal Chem* 1996, 518, 21.
50. Rebolledo, A. P.; Ardisson, J. D.; De Lima, G. M.; Macedo, W. A. A.; Beraldo, H. *Hyperfine Interactions* 2005, 163, 89.
51. Yasuda, M.; Hayashi, K.; Katoh, Y.; Shibata, I.; Baba, A. *J Am Chem Soc* 1998, 120, 715.