

## Thiirane Resins Cured with Polythiourethane Hardeners as Novel Supports for Metal Complex Catalysts

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**ABSTRACT:** The application of thiirane resin cured with polythiourethane (PTU) hardeners as novel and efficient support for palladium complex catalyst is reported. Stability and activity efficiency in Heck reactions were determined. IR and X-ray photoelectron spectroscopy provided information of metal coordination to the polymer matrix. Characterization of polymer supports and palladium catalysts has involved the measurements of the structural parameters in the dry state by the nitrogen BET adsorption, time-of-flight secondary ion mass spectrometry, scanning electron microscopy, and energy dispersive X-ray analysis. The results of this study indicate that PTU used to cure thiirane resin can greatly affect the catalytic properties of the episulfide resin-supported palladium catalyst. These new type of polymer supports comparing to other organic carriers offers several practical advantages such as ability to control the crosslinking density, porosity and the chemical structure of the polymeric matrix, which influence the catalytic properties of the immobilized metal complex. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40330.

**KEYWORDS:** catalysts; properties and characterization; resins; structure-property relations; thermosets

Received 27 September 2013; accepted 17 December 2013

DOI: 10.1002/app.40330

### INTRODUCTION

Recently, there has been a growing interest in exploring transition metal complex catalysts immobilized on polymeric organic matrices.<sup>1–3</sup> Polymer-supported transition metal complexes have started to be looked at as an good alternative to typical inorganic carriers. The main advantage of polymer supports is the chemical, physical and morphological structure of these materials and its influence on the catalytic properties of the metal complex immobilized on it. Easy separation and recovery of the immobilized catalysts together with the high activity and selectivity comparable to those of soluble metal complexes is the most important point in the study.

Although the polymerization process of epoxy resins using the opening of the epoxide ring creates many possibilities for easy functionalization, there have been only few reports on the use of epoxy resins as supports of metal complex catalysts in organic synthesis. The use of epoxy resins as carriers of catalysts has been limited so far to the use of the metal complex as the polymerization initiator and the precursor of the catalytic centers in the cured resin and the application of various matrices functionalized with epoxy groups for the immobilization of proteins and enzymes to improve their biocatalytic properties.<sup>4–6</sup>

Thiol-functionalized epoxy have proved to be very convenient to stabilize enzymes via multipoint immobilization. Their use allowed not only the specific immobilization of enzymes through their thiol groups via thiol-disulfide interchange, but also enzyme stabilization via multipoint covalent attachment.<sup>7</sup> In our earlier works, we used bisphenol epoxy resin cured with ammonium ionic liquids as support for palladium complex catalyst.<sup>8</sup> The usage of ionic liquids as hardeners for epoxy resins could greatly affect the activity of the catalyst without necessity of additional functionalization to improve of ligand-binding affinity to metal complexes. Investigated catalysts showed good selectivity during prolonged use in the Heck reaction.

Epoxy resins have good mechanical properties, but their long low temperature curing time limits their potential is in many industrial applications. The thiirane (episulfide) resins, sulfur analogues of epoxides, have been used advantageously in the polymer industry, for low-temperature rapid curing application.<sup>9–14</sup> The C–S bond is longer than the C–O bond, the episulfide ring has lower cyclic strain in comparison with the oxirane ring. The polarity of the C–S bond is smaller than that of the C–O bond. The electron density at the oxygen atom in

oxiranes is higher than that at the sulfur atom in thiiranes. Hence, thiiranes are less reactive toward electrophilic reagents than oxiranes, and have about the same or a little higher reactivity. In addition, in nonionic reactions involving ring cleavage thiiranes are more reactive than oxiranes. Obviously, the lower ring strain is overruled by the lower bond energy of C—S compared with C—O bonds.<sup>15</sup> As a result, thiirane resins exhibit higher activity in ring opening reactions than epoxides. Addition products of oxirane and thiirane rings with a amine hardeners, are —OH and —SH groups, respectively. Because thiol has a higher reactivity than that of alcohol, episulfide resins (ESR) can be cured at temperatures much lower than that of the conventional epoxy resins, so the introduction of ligands onto ESR is as simple as for the oxirane analogue.<sup>14</sup>

Given the easy coordination ability of the thiol group, we decided to extend our studies on catalyst supports based on functionalized epoxy resins to episulfides. Such resins were found to have a high capacity and selectivity towards metal-ion species and would present enormous potential for the production of novel functional resins, for such applications as metal complex catalyst matrices or metal ion exchangers. For example, a sulfur analogue of the glycidyl methacrylate (GMA-S) resin was synthesized by Moore et al.<sup>16</sup> In this polymer, the oxirane group was replaced by a thiirane ring. The ring-opening reaction of the pendant thiirane group with amines or other nucleophiles generates a thiol group at the  $\beta$ -carbon atom. Such immobilization of ligands produces ion-exchange resins, which may be used in waste-water treatment and in regeneration of metal salts in industrial processes. Whether in these ion-exchange resins the metal binds not only ligand, but also thiol group takes part in metal-ion binding, thereby acting as additional donor site. Also Berkel et al. prepared ion-exchange materials from a thiirane GMA-based polymer functionalized with azole and benzimidazole ligands. These resins were selective for  $\text{Cu}^{2+}$  under competitive conditions over a range of other divalent transition metal ions.<sup>17,18</sup>

Herein, we reported the results of our preliminary works on the synthesis of some efficient heterogenized palladium catalysts based on supports prepared from thiirane resin cured with thiol-terminated polythiourethanes (PTU). These novel effective curing agents were synthesized from low-molecular-weight difunctional and multifunctional mercaptans and diisocyanates.<sup>19</sup> The oligomeric PTU apart from their good curing characteristic of epoxides, allow to introduction of new binding ligands into structure of polymer. Our aim was to evaluate the usefulness of ESR-immobilized palladium catalysts for the Heck reaction, to look at the effect of a polymer morphological structure on the catalytic activity, and to assess the catalyst stability.

## EXPERIMENTAL

### Materials

All organic reagents used in this study were supplied from Sigma-Aldrich and were used as received without further purification. The commercially available epoxy resin (diglycidyl ether of bisphenol A) *Epidian-5*, having epoxide number of 0.487 was obtained from Organika-Sarzyna, Poland. The viscosity of the resin is  $23.9 \text{ N s m}^{-2}$  at  $25^\circ\text{C}$ .

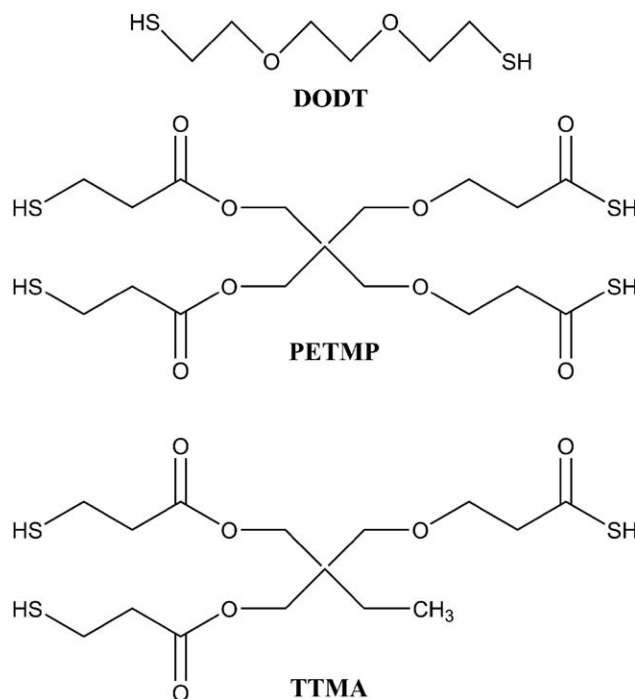


Figure 1. Structure of mercaptan monomers.

### Synthesis of Episulfide Resin

A modification of the synthesis method originally employed by Bell was followed in this work.<sup>20</sup> Episulfide resin was synthesized from the reaction of epoxy resin (*Epidian-5*) and thiourea. A solution of 0.15 molar equivalents of epoxy resin in 200 mL of methanol/THF (5/1 vol) was prepared in a 0.5 L 3-necked flask equipped with mechanical stirrer. To this solution, 0.225 molar equivalents of thiourea in 200 mL of methanol were added dropwise at room temperature over a period of 2 h. Afterwards, the mixture was stirred at temperature of  $50^\circ\text{C}$  for 20 h, and then poured into 150 mL of cold distilled water. After 3 h, the white precipitate of ESR was washed three times with methanol/water (2/1 vol) mixture and air dried. The crude product was then dissolved in 200 mL of methylene chloride, washed three times with distilled water and dried over anhydrous magnesium sulfate for 24 h. The solid ESR was filtered off and dried under vacuum. Overall yield of 90%, based on starting epoxide, was obtained. The structure of thiirane resins was confirmed by Fourier transform infrared spectroscopy and elemental analysis.

IR (neat),  $\nu$  ( $\text{cm}^{-1}$ ) 3500, 3057, 2965, 1608, 1508, 1049 (stretching C—S of thiirane ring), 1035, 916 (stretching C—O of oxirane group), 862 (stretching C—O—C of oxirane group), 617 (stretching C—S—C of thiirane ring), 772. Anal. calcd for 100% conversion of epoxy resin: C: 71.44%, H: 6.51%, O: 13.32%, and S: 8.73%; found: C: 72.13%, H: 6.57%, O: 14.42, and S: 6.88%.

### Synthesis of PTU

PTU were prepared by the reaction of hexamethylene diisocyanate (HDI) and particular mercaptan: 3,6-dioxo-1,8-octanedithiol (DODT), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), trimethylolpropane tris(3-mercaptopropionate)

(TTMA), (Figure 1). Details of their synthesis and characterization of chemical structure have already been described in our previous article.<sup>19</sup>

### Preparation of the Carriers

The carrier was prepared by mixing the episulfide resin (5 g) with the PTU hardener (20 wt %). After obtaining homogenous consistency, the mixture was transferred onto a Teflon® mold and cured at a room temperature over a period of 1–2 h. For all cured samples, 0.01% of 2,4,6-tris(dimethylaminomethyl)-phenol (DMP-30) was used as an accelerator.

### Preparation of the Catalysts

The cured resin was then mechanically ground to a powder. On the prepared support, we immobilized the palladium complex  $\text{PdCl}_2(\text{PhCN})_2$  from toluene solution, by ligand-exchange process. For all supported catalysts, the Pd content was fixed below the metal uptake capacity for a polymer ( $\sim 0.140 \text{ mM g}^{-1}$ ), what was confirmed by AAS analysis of the colorless toluene solutions after immobilization process.

### Catalyst Test

The typical Heck reaction was carried out in 50 mL laboratory reactor. The reactor was charged with 0.05 g of supported palladium catalyst, 0.28 mL of iodobenzene, 0.23 mL of methyl acrylate, 0.15 mL of toluene, 0.35 mL of triethylamine and 1.00 mL of *N*-methylpyrrolidone. The reaction was conducted at a temperature of 80°C for 1.5 h. Samples were taken every 5, 15, 30, 60, and 90 min. The products of Heck reaction were quantitatively analyzed by gas chromatography (GC) on a Hewlett-Packard 5990 II gas chromatograph equipped with a thermal conductivity detector. The GC column was HP-50+ (crosslinked 50% Ph Me silicone) 30 m  $\times$  0.63 mm  $\times$  1.0  $\mu\text{m}$  film thickness. Injector and detector temperature: 210°C. Carrier gas: helium. Temperature program: the column was kept in 50°C for 2 min, and then heated to 150°C at a rate of 5°C/min. The product was identified by matching retention times with those of authentic samples. The only observed product in all conducted reactions was the methyl *trans*-cinnamate.

### Mercury Test

The mercury poisoning experiment was performed using 500-fold excess of Hg(0) relative to palladium catalyst. Polymer-supported catalyst was vigorously stirred with mercury for 24 h prior reaction. The same experiment was also conducted as reference, using as catalyst homogeneous precatalyst complex,  $\text{PdCl}_2(\text{PhCN})_2$ . In this case, Hg(0) was introduced at the beginning, together with other reactants.

### Gel Permeation Chromatography (GPC)

Molecular weight ( $M_n$  and  $M_w$ ) were measured by GPC using a HP 1100 series liquid chromatograph, equipped with PLgel 5 $\mu$  Mixed-C column. Tetrahydrofuran was used as an eluent at flow rate 0.5 mL  $\text{min}^{-1}$ . Standards polystyrenes (Fluka) having  $M_w$  in the range of 400–2,000,000 g  $\text{mol}^{-1}$  were used as references for molecular weight evaluation.

### Morphology Studies

Pore size distribution parameters were determined by application of the BET method on Sorptomatic 1900 FISONS Instru-

**Table I.** Molecular Weight Distribution of PTU

Mercaptan monomer	Polymer abbreviations	Molecular weight, $M_n$ (g/mol)	Molecular weight, $M_w$ (g/mol)	PD
DODT	DODT-HDI	3002	4937	1.48
TTMA	TTMA-HDI	4875	5831	1.17
PETMP	PETMP-HDI	5104	5692	1.13

ment. Energy dispersive X-ray microscope [scanning electron microscopy (SEM)–energy dispersive X-ray analysis (EDX)], JEOL JSM 840A, Japan, was used to observe the elemental distribution. The white points in the figures denote Pd atoms.

### Study of Pd Leaching

The amount of palladium loaded in the support was analyzed by atomic absorption spectroscopy (AAS) method with a Perkin Elmer 3030 atomic absorption spectrometer. A sample of a polymer supported catalyst was heated up to 600°C and then dissolved in aqua regia. The resulting solution was diluted and assayed by AAS. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed using an ION-TOF GmbH instrument (TOF-SIMS IV) equipped with 25 keV pulsed  $\text{Bi}^+$  primary ion gun in the static mode (primary ion dose about  $1.5 \times 10^{11}$  ions  $\text{cm}^{-2}$ ). The analyzed area corresponds to a square of 500  $\times$  500  $\mu\text{m}$  in the case of secondary ion mass spectra collecting and surface imaging. For each sample, three spectra from different surfaces areas were detected. To obtain the plain surface of catalysts (then better mass resolution could be achieved), powder samples were tableted before the measurements. In order to compare the quantity of palladium present on the surface of “fresh” and “used” catalysts, the number of counts of selected ions obtained from collected mass spectra was normalized on the basis of the value of total counts.

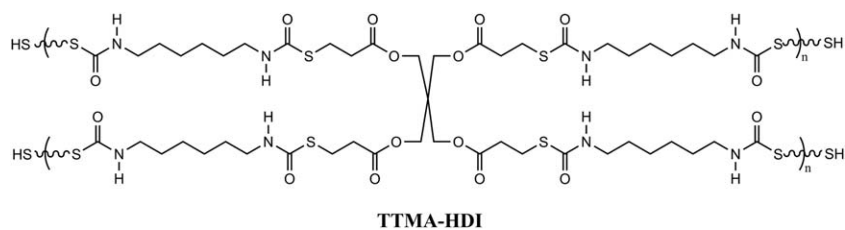
### Spectroscopy Characterization

The FT-IR spectra were measured by BIORAD 175C spectrophotometer in an air atmosphere. XPS measurements were made on a VG ESCALAB 210 spectrometer with Mg K  $\alpha$  ( $h\nu = 1253.6 \text{ eV}$ ) excitation from an X-ray tube (reduced power 10 kV, 10 mA). The pressure in the spectrometer chamber was about  $5 \times 10^{-9}$  mbar. Samples were pressed to pellets under a pressure of 100 kbar for 10 min before these measurements. The S 2p, N 1s, O 1s, Cl 2p, and Pd 3d core level spectra were recorded. The analyzer pass energy was set at 20 eV. A take-off angle of 90° was used in all XPS studies. Curve fitting was performed using the ECLIPSE data system software. This software describes each of the components of a complex envelope as a Gaussian-Lorentzian sum function. The background was fitted using non-linear model function proportional to the integral of the elastically scattered electrons (Shirley backgrounds). All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Palladium Catalysts

In recent years, modification of organic polymers with catalytically active species are considered as one of the most versatile



**Figure 2.** Structure of TTMA-HDI PTU.

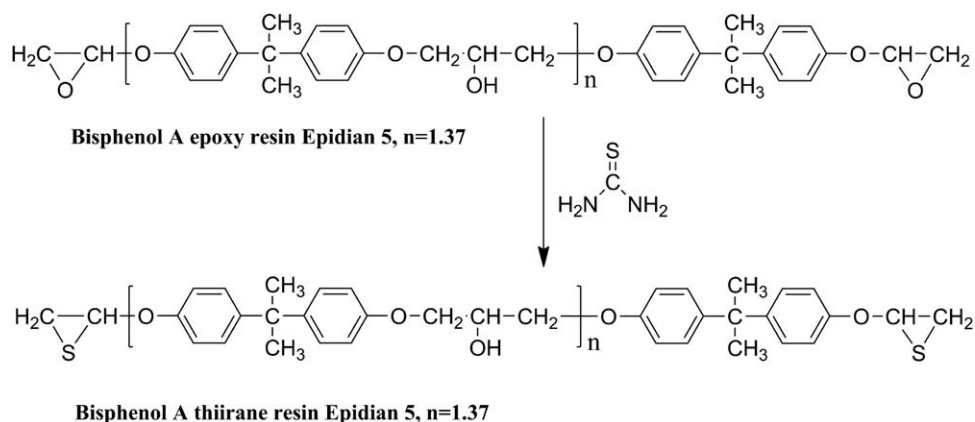
strategies for the development of efficient catalyst systems. By converting multifunctional mercaptans (difunctional, trifunctional, and tetrafunctional) presented in Figure 1 into corresponding PTU, we received efficient curing agents for epoxy resins.<sup>19</sup> Molecular weight data of PTU obtained by GPC are presented in Table I. Figure 2 presents the structure of PTU obtained from TTMA and HDI.

To increase binding ability of metal complex catalysts with functional resin, we decided to use these hardeners for curing ESR. The initial comparison tests of palladium catalysts supported on epoxy and thiirane resins cured with PTU resins revealed that episulfide supports have higher metal uptake capacity and provide higher activity of catalysts than epoxy-supports. Palladium complex uptake was estimated by observing color change of catalyst precursor solution during immobilization process. It was about two times higher in the case of thiirane resins than for epoxides, both cured with PTU. This indicates the importance of thiol groups released by opening of episulfide rings, in binding of metal complex. Thiirane resins were synthesized by replacement of oxygen atoms bisphenol A epoxy resins (*Epidian 5*) with sulfur atoms using thiourea (Figure 3). Under the optimized reaction conditions, a high conversion of epoxide into ESR was achieved. Due to similar structures of oxirane and thiirane rings the analysis of the conversion of epoxy resin is difficult. We applied, quantitative analysis of conversion of epoxy groups by FTIR spectra, propose by Li and Cheng.<sup>21</sup> The product of the reaction was a mixture of epoxy resin and thiirane resin, with 78% of thiirane unit.

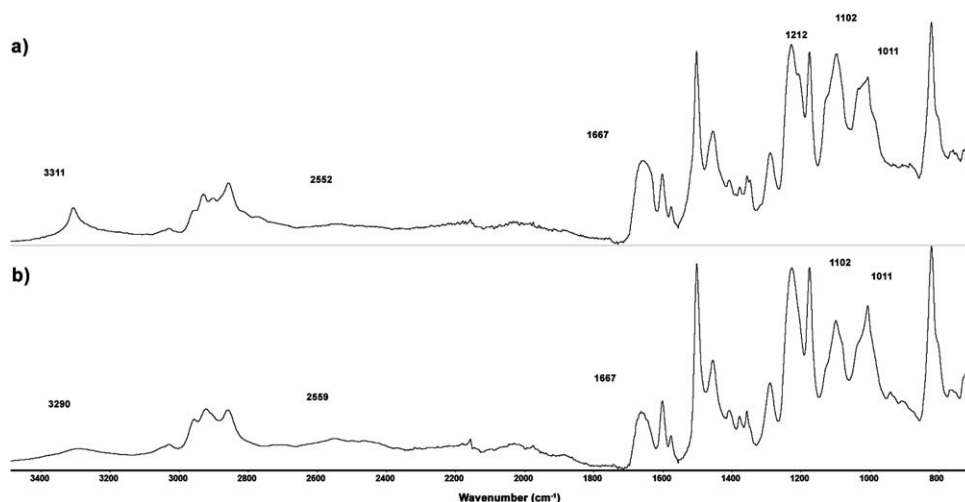
By the incorporation of the thiourethane group ( $-\text{SC}(\text{O})\text{NH}-$ ) to the ESR matrix, we received a polymer support with ligands able to chelating the palladium complex. Additional, binding

ligands in the form of thiol groups were introduced after ring opening of the thiirane moieties. Generally, thiiranes show lower reactivity toward mercaptans than oxiranes in the absence of catalysts.<sup>15</sup> However, in the presence of high-basicity DMP-30 amine accelerator, we found that all episulfide rings were opened during cross-linking process, what was confirmed by IR-spectroscopy. This procedure leads to an easy and controlled insertion of bonding groups to the polymeric structure, without further resin functionalization. The metal complex was introduced to the matrix via ligand exchange reaction with palladium precursor  $\text{PdCl}_2(\text{PhCN})_2$ .

To confirm the structure of received supports and catalysts the FTIR spectroscopy was used. Figure 4 shows IR spectra of ESR cured with DODT-HDI PTU hardener and palladium catalyst supported on it (ESR/DODT-HDI/Pd). The lack of characteristic oxirane and thiirane bands (symmetric ring deformation), respectively, at  $916$  and  $1049\text{ cm}^{-1}$ , indicates that reaction of epoxy and ESR rings was complete. The reaction of the amine accelerator or thiol terminated PTU hardener with oxirane ring produces hydroxyl group. This is capable of further reaction to ring-open more epoxy and thiirane groups to give ether linkages. Disappearance of  $1212\text{ cm}^{-1}$  absorption band (C—O—C stretching) after complexation, shows that ether moiety, can interact with transition metal. The shifts and clear changes in the intensity of characteristic absorption bands of thiourethane group, at  $1102\text{ cm}^{-1}$  (C—N stretching),  $1667\text{ cm}^{-1}$  (C=O stretching),  $3311\text{ cm}^{-1}$  (N—H stretching) after catalyst immobilization, suggest that thiourethane moiety is the main active center of polymer network, which participate in coordination of metal by nitrogen and oxygen atoms. The shift of the absorption peak of S—H vibration, from  $2552\text{ cm}^{-1}$  in ESR/DODT-



**Figure 3.** Synthesis of thiirane resin from epoxy resin.



**Figure 4.** FT-IR analysis of the thiirane resin cured with DODT-HDI PTU: a) pure resin; b) after immobilization of  $\text{PdCl}_2(\text{PhCN})_2$ .

HDI to  $2559\text{ cm}^{-1}$  in ESR/DODT-HDI/Pd, indicating that mercapto groups, released by thiirane ring opening, were also bound to the lead palladium. However, the characteristic vibration of the Pd-S bond cannot be detected in the FTIR spectrum.

XPS analysis were carried out to study the binding mechanism of Pd(II) to the polymer matrix. Table II shows the electron

BEs (eV) of the episulfide resin cured with all studied PTU supports before and after immobilization of Pd complex. ESR/PTU/Pd catalysts were characterized both prior to and following their use in the Heck reaction. Their XPS spectra exhibited two dominating peaks of Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  typical for Pd(II). For further discussion, only Pd  $3d_{5/2}$  peak is shown. The XPS data are consistent with FTIR measurements and show that multiple possible coordination sites participate in binding the

**Table II.** BE Values for Supported Palladium Catalysts and Pure Polymer Supports

Sample	BE (eV) <sup>a</sup>							
	Pd $3d_{5/2}$			N 1s	O 1s	S 2p		Cl $2p_{3/2}$
Pd(II)	Pd(0)	Pd <sup>δ+</sup>	C-S-C			-SH		
ESR/DODT-HDI				400.1	532.8	164.3 (32)	163.2 (68)	
ESR/DODT-HDI/Pd (before use)	337.9 (100)			401.4	536.2	164.9 (33)	163.7 (67)	201.8
ESR/DODT-HDI/Pd (after first use)	337.7 (61)	336.5 (4)	335.3 (35)	401.5	536.1	164.8 (33)	163.6 (67)	201.6
ESR/DODT-HDI (after seventh use)	337.1 (53)	336.2 (7)	335.0 (40)	401.6	536.0	164.7 (34)	163.6 (66)	201.6
ESR/PETMP-PETMP				400.0	533.1	164.2 (52)	163.1 (48)	
ESR/PETMP-HDI/Pd (before use)	337.8 (100)			401.2	535.9	164.5 (54)	163.8 (46)	201.8
ESR/PETMP-HDI/Pd (after first use)	337.7 (90)	336.7 (1)	335.4 (9)	401.4	535.8	164.6 (54)	163.8 (46)	201.7
ESR/PETMP-HDI (after seventh use)	337.5 (74)	336.8 (3)	335.6 (23)	401.3	535.9	164.7 (55)	163.7 (45)	201.8
ESR/TTMA-HDI				400.2	532.9			
ESR/TTMA-HDI/Pd (before use)	337.7 (100)			401.5	536.4	164.8 (48)	163.9 (52)	201.8
ESR/TTMA-HDI/Pd (after first use)	337.8 (78)	336.9 (7)	335.9 (15)	401.4	536.5	164.7 (49)	163.7 (51)	201.6
ESR/TTMA-HDI (after seventh use)	337.6 (69)	336.7 (9)	335.4 (22)	401.6	536.6	164.9 (50)	163.8 (50)	201.6

<sup>a</sup> Values in brackets indicates the shares of individual peak components (%).

**Table III.** Characteristics of Episulfide Supports by the BET Methods

ESR	ESR/ DODT-HDI	ESR/ TTMA-HDI	ESR/ PETMP-HDI
Mean pore diameter (nm)	1.6	25	40
Volume of pores (%)			
Macro $w > 50$ nm	2.1	9.6	15.3
Meso $2 < w < 50$ nm	18.4	59.3	68.7
Micro $w < 2$ nm	79.5	31.1	16.0
Pore specific volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.09	0.17	0.21
Porosity	0.11	0.19	0.23
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	75	110	165

Pd to the PTU-cured episulfide support. This is indicated by the increase of the BE for thiourethane nitrogen atoms and  $\text{O}_{\text{C=O}}$  1s electrons after the Pd attachment. The electron BEs of S  $2p_{3/2}$  show a doublet signal in the range of 163.1 and 164.9 eV, which is assigned to two types of sulfur type ligands. The shift of these signals in the spectrum of catalyst to higher value of BE is accounted for by coordination of Pd through thiol group and sulfur atom of thiourethane moiety. XPS spectra of the freshly prepared ESR/PTU/Pd catalyst show that palladium appears dominantly in the form of Pd(II). The recovered ESR/PTU/Pd catalysts after a Heck reaction contained  $\text{Pd}^{\delta+}$  nanoclusters and also some minor fraction of Pd(0). The amount of these species increases after subsequent use of the catalyst. It indicates that episulfide matrix might stabilize such catalytically active monovalent metastable Pd forms. Since the ESR cured with PTU possesses coordination sites of different coordination ability, it seems very likely that the zero-valent palladium, Pd(0), comes from reduction of Pd(II) coordinated to the carbonyl oxygen, the weaker of the possible coordination sites, whereas new formed after each reaction run, Pd clusters, comes from the reduction of Pd(II) coordinated to the sulfur or nitrogen atoms. Similar Pd states were found before for the epoxide-supported palladium complexes.<sup>5</sup> The formation of Pd(0) fraction can be also explained by partial oxidation of Pd-nanoparticles trapped in the crosslinked resin.<sup>22</sup> The observed at XPS spectra BE of Cl  $2p_{3/2}$  in the region of 201.7–201.9 eV indicates the presence of  $-\text{PdCl}_2$  structure. Further investigations of the chemical structure of catalyst and the nature of metal coordination to the polymer matrix, including spectroscopic characterization of low-molecular-weight model ligands in the far-infrared region, will be reported at a later stage.

### Porous Structure Studies

The catalytic performance of polymer supported catalysts depends on both the nanoenvironment surrounding the active centers and their accessibility. The nanoporosity of the polymer support can affect the concentration of reagents and products inside of micropores with potential influence on catalytic activity and selectivity. In addition, the structure of the catalytic species strongly depends on the microporous morphology of the support. During repeating use of catalysts, we observed the generation of the nanoclusters

within the polymer. The growth of the metal nanoparticles becomes limited by the steric restrictions imposed by support nanoscale morphology. The results determined by nitrogen BET adsorption method indicate that investigated supports have different pore size distribution, which probably arise from differences in their crosslink densities (Table III). The thiirane resins ESR/TTMA-HDI and ESR/PETMP-HDI show pore size distribution with the lower volume of micropores compared with the ESR/DODT-HDI support. The mesopores of these catalysts were concentrated in a narrow band, respectively,  $\sim 25$  and  $\sim 40$  nm in diameter. The lower surface area ESR/DODT-HDI polymer had pore size distribution with the majority of the micropores  $\sim 1.6$  nm. SEM images of Pd-supported catalysts confirmed such surface morphology (Figure 5). SEM images of ESR/TTMA-HDI and ESR/PETMP-HDI resins clearly show the presence of abundant large pores.

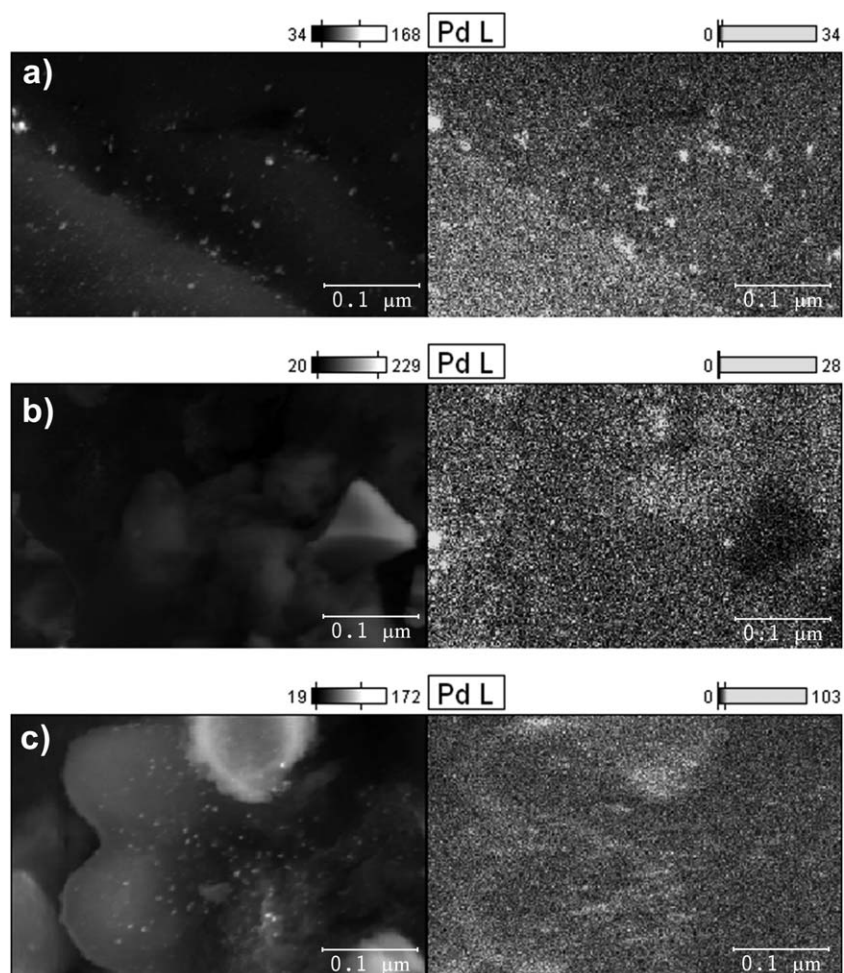
### SEM-EDX Studies of Pd Catalysts

The characterization of palladium distributions on the surface of catalysts and nanoparticles size distributions were performed with SEM and energy-dispersive X-ray spectroscopy (EDX) for samples of catalysts after seventh use (Figure 5). From presented SEM-EDX images of catalysts it is difficult to precisely characterize Pd clusters or nanoparticles. However, X-ray microprobe showed that Pd is homogeneously dispersed throughout the particles of the ESR/TTMA-HDI/Pd and ESR/PETMP-HDI/Pd catalyst, suggesting the pore structure in these samples is not favorable for stabilization of Pd nanoparticles [Figure 5(b,c)], Visible agglomerates of Pd (2–15 nm) dispersed on the surface of the ESR/DODT-HDI resin [Figure 5(a)] indicate that different metal particle size distribution was influenced by morphology of this support and can be also an explanation for the unequal catalyst performances.

### Activity and Stability Tests

The activity and stability of the palladium catalysts were tested during a multiple use in the model Heck reaction (Table IV). The reaction entailed coupling of iodobenzene with methyl acrylate, occurring in the solution of *N*-methylpyrrolidone (NMP) in the presence of triethylamine (Figure 6). In the reaction, which were conducted with all prepared heterogenized catalysts, the only observed product was the methyl *trans*-cinnamate. The catalytic activity is lower for catalyst showing the lowest volume of micropores (ESR/TTMA-HDI/Pd, ESR/PETMP-HDI/Pd). Such surface morphology enables us to achieve a fine dispersion of the metal without larger Pd nanoparticles, even after prolonged use of catalyst. Indeed, the XPS analysis showed the presence of the Pd(II) state in these catalyst. In contrary, for more active ESR/DODT-HDI/Pd reused catalyst, we observed greater content of Pd(0) and  $\text{Pd}^{\delta+}$  valence states, so it can be supposed that microporous matrix of ESR/DODT-HDI resin plays the role of stabilizers of formed nanoparticles, which are generally considered the catalytic active form in Heck coupling. There are many reports in the literature indicating that the catalysts containing a mixture of valence states of Pd(II), Pd(0), and  $\text{Pd}^{\delta+}$  alone, are more active than Pd(II) catalysts.<sup>23,24</sup>

The activities of all tested catalysts only slightly decreased with the subsequent usage, which might be caused by the palladium



**Figure 5.** SEM micrograph and EDX Pd-mapping of the surface of episulfide resin-supported palladium catalysts after seventh use.

**Table IV.** The Catalyst Activity in Heck Reaction

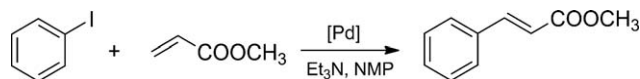
Catalyst	Run	Conversion <sup>a</sup> (%)	Pd content <sup>b</sup> (g/g)	<sup>106</sup> Pd <sup>+</sup> intensity <sup>c</sup>
Homogeneous catalyst, PdCl <sub>2</sub> (PhCN) <sub>2</sub>	1	98		
ESR/DODT-HDI/Pd	1	96	0.0138	$0.8 \times 10^{-3}$
	3	92	–	–
	7	89	0.0082	$0.5 \times 10^{-3}$
ESR/TTMA-HDI/Pd	1	83	0.0142	$1.3 \times 10^{-3}$
	3	79	–	–
	7	74	0.0095	$0.9 \times 10^{-3}$
ESR/PETMP-HDI/Pd	1	81	0.0150	$1.8 \times 10^{-3}$
	3	78	–	–
	7	76	0.0126	$1.4 \times 10^{-3}$

<sup>a</sup> Conversion of iodobenzene after 1.5 h.

<sup>b</sup> The amount of palladium loaded in the support was determined by AAS method.

<sup>c</sup> Normalized intensity of <sup>106</sup>Pd<sup>+</sup> selected from the mass spectra of palladium catalysts (TOF-SIMS).

Reaction conditions: temperature 80°C; substrates: iodobenzene 0.28 mL (2.5 mmol), methyl acrylate 0.23 mL (2.5 mmol); solvent: toluene 0.15 mL (1.4 mmol), triethylamine 0.35 mL (2.5 mmol), *N*-methylpyrrolidone (NMP) 1.00 mL (10.4 mmol); supported catalyst: 0.05 g; the conversion refers to GC analysis. The only observed product was the methyl *trans*-cinnamate.



**Figure 6.** The Heck reaction of iodobenzene with methyl acrylate.

leaching. To monitor the deactivation process TOF-SIMS and AAS were used. Catalysts after seventh use were analyzed and compared to the fresh samples. In all cases, a small drop of the amount of surface accessible palladium was observed however, the drop of Pd content did not significantly affect the catalyst activity, which can be another proof of higher activity of palladium nanoparticles generated in reused catalysts. (Table IV).

As additional evidence for the identity of the true catalyst, hot filtration technique and poison with Hg(0) of catalysts has also been employed. To check whether immobilized or leached palladium was responsible for the observed catalytic activity, the hot filtration test was performed.<sup>25</sup> The Heck reaction was stopped after 5 min, when conversion of iodobenzene reached 50%. Next, the solution was separated from the catalyst by filtration, and the reaction continued for 60 min. After that time, the conversion of iodobenzene increased only to 56%, what indicating that the solution had contained only a trace amount of catalytically active soluble palladium species, what was confirmed by AAS measurements (not presented here).

To rule out the possibility of catalysis by microparticles (nanoclusters) of zero-valent palladium formed from leached and reduced Pd(II) precursor, a mercury poisoning experiment was carried out by adding mercury to the reaction mixture before the catalytic test. The mercury poisoning of metal(0) particles is a widely used test for the heterogeneity/homogeneity of catalysis.<sup>26</sup> It is known that trace amounts of leached metal particles or soluble palladium complex can be very catalytically active.<sup>27</sup> Episulfide-supported palladium catalyst vigorously stirred with large excess of mercury for 24 h prior reaction, shows almost the same catalytic activity for Heck reaction as before poisoning. In addition, mercury poisoning test for reaction catalyzed by homogeneous precatalyst complex, PdCl<sub>2</sub>(PhCN)<sub>2</sub>, was performed as reference. In this case, addition of Hg(0) to the homogeneous reaction solution completely suppressed the catalytic activity, indicating that molecular species detached from support are not the catalytically active sites. Thus, filtration test and poisoning results suggest that catalysis is not associated with leached precursor complexes or *in situ* formed palladium nanoclusters, which would redeposit to the polymer support after the reaction.

The prepared catalysts are air stable and after 6 months are still active as a freshly prepared sample. The catalytic systems immobilized on PTU-cured episulfides, including also platinum complexes, are currently the subject of our further investigation in hydrogenation of unsaturated aldehydes.

## CONCLUSION

Novel supports for metal complex catalysts were prepared. Thiirane resins cured with PTU hardeners are very useful and versatile polymeric supports for preparation of heterogenized palladium catalysts for Heck reaction. The use of polythioure-

anes as curing agents enables to obtain supports, which do not need any further functionalization. The different coordination sites in the polymer promote the formation of active catalytic species mainly as finely dispersed metal particles with mixed valence states. The chemical structure of used PTU oligomers can greatly affect the activity of the catalysts. The activity of the catalysts was comparable to that of homogeneous PdCl<sub>2</sub>(PhCN)<sub>2</sub>. Some differences in activity were caused by differences in the chemical structure of the support, as well as the disparate impact of surface morphology of supports cross-linked with different type of PTUs on the size distribution of catalytically active palladium nanoparticles generated on the surface of the resin during prolonged use of catalyst. Moreover the stability and very good recycling efficiency of these catalysts make them useful for prolonged use. These supports unlike to their inorganic and common polymeric counterparts, can be easily prepared into a range of forms and shapes like membranes, beads, films or powders, to facilitate the catalyst separation from reaction mixtures and their recycling. Future work will be devoted to the application of these supports for immobilization of other transition metal complexes and to prepare catalysts for other reactions.

## ACKNOWLEDGMENTS

This work was supported by the National Science Centre (Poland) (grant No 0255/B/H03/2011/40).

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