Preparation, spectroscopic and catalytic studies of poly(1,4-phenylene-methylidynenitrilo-1,4-phenylenenitrilomethylidyne) protonated with selected heteropolyacids

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Abstract

Poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne), (PIM), i.e. polyimine obtained via condensation of p-phenylenediamine and terephtalaldehyde, has been prepared and protonated with selected Keggin type heteropolyacids ($H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$). Both, unprotonated and protonated PIM have been characterized by IR spectroscopy, X-ray diffraction measurements and thermal studies. Heteropolyacids inserted into PIM matrix preserve their structural identity. PIM–heteropolyacids systems exhibit high thermal stability. They are catalytically active in isopropanol conversion showing enhanced redox activity.

Keywords: Polyimines; Conjugated polymers; Heteropolyanions; Catalysis

1. Introduction

Extensive research has been carried out on conjugated polymers for the last two decades. This research has been stimulated mainly by extremely interesting electronic and optical properties of these compounds. In particular, upon appropriate doping, several conjugated polymers can be transformed into organic conductors exhibiting conductivities approaching those of metals [1–3].
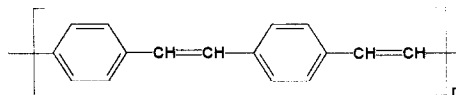
Poly(p-phenylene vinylene) and its ring-substituted derivatives are of special interest. In the doped state these compounds exhibit high conductivity whereas in the undoped state they

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show strong electroluminescence with spectral characteristics dependent on substituent [4].
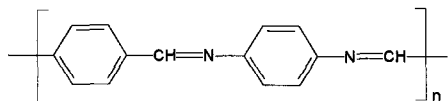
Poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) (PIM) is isoelectronic with poly(p-phenylene vinylene). Both unsubstituted PIM and its ring-substituted derivatives show interesting non-linear optical properties and in recent years they have been subject of intensive research concerning their preparation and characterization [5–8].

Contrary to poly(p-phenylene vinylene) PIM contains basic sites of imine nitrogen type. Thus, similarly as polyaniline PIM can be doped via the protonation reaction. This doping of acid–base type enables the introduction of anions of desired optical, magnetic or catalytic properties to the polymer matrix.

Several research groups have used conjugated polymers as convenient matrices to which heteropolyanions can be incorporated mainly via electrochemical doping [9–12].

The application of conjugated polymers doping reaction to the preparation of a new generation of conjugated polymer supported heterogeneous catalysts has been initiated in our research group. In particular heteropolyanions of Keggin-type have been successfully inserted to polyacetylene and polypyrrole via oxidative doping [13,14] and to polyaniline via the protonation reaction (acid–base doping) [15–17].

Following our previous experience, in the present research we have used the reaction of PIM protonation for the preparation of polyimine supported heterogeneous catalysts containing Keggin-type heteropolyanions.

2. Experimental

The following chemicals and reagents have been used for the synthesis of the polymer and for its protonation: p-phenylenediamine 97% (Aldrich), terephtalaldehyde 98% (Fluka), acetic acid (pure, for analysis Z.A. Oswiecim), sodium acetate (pure, POCh S.A. Gliwice), DMF (pure, MZRP Plock), $H_3PMo_{12}O_{40}$ (Merck), $H_3PW_{12}O_{40}$ (Aldrich), acetonitrile (spectroscopic grade Merck).

PIM has been prepared from p-phenylenediamine and terephtalaldehyde using a modification of the method described in [18].

Freshly recrystallized p-phenylenediamine (5.4 g) was refluxed with 6.7 g of recrystallized terephtalaldehyde in a solution of 10 g of anhydrous sodium acetate in 35 ml of glacial acetic acid. Bright yellow polymer precipitated instantaneously and the mixture was refluxed for 2 h. The precipitate was separated from the solution, then it was refluxed in 250 ml of dimethylformamide to dissolve unreacted monomer and condensation products of low molecular weight. The polymer was then washed with acetone and dried in vacuum for 3 h.

The protonation of polyimine with heteropolyacids (HPA) has been carried out at room temperature in 0.02 M acetonitrile solutions, typically for 5 h. The protonation level can be conveniently varied by changing the molar ratio of PIM:heteropolyacids in the protonating medium.

HPA protonated samples have been characterized by elemental analysis, FTIR spectroscopy, X-ray diffraction and thermogravimetric (TG) measurements.

In the catalytic studies, isopropanol conversion has been used as the test reaction. Catalytic tests have been carried out in a wide temperature range using a differential reactor described elsewhere [19]. Neutral, oxygen-free atmosphere was used and the reactant (isopropanol) was diluted to the concentration of 1.45 mol%. The reaction products were analyzed using a gas chromatograph equipped with a FID detector, acid-resistant column 4 mm i.d. and 4 m long packed with 4% Carbowax 20M on Chromosorb G, AW, DMCS mesh 80/100.

3. Results and discussion

The reaction of powdery polyimine with heteropolyacids dissolved in acetonitrile results in the incorporation of heteropolyanions to the polymer matrix via the protonation reaction. The protonation of the imine site of the polymer is clearly manifested in N1s XPS spectra by the appearance of a peak at 401.5 eV characteristic of charged nitrogen atoms [18].

The amount of heteropolyanions introduced to the polymer matrix via the protonation reaction has been determined by elemental analysis and more precisely from analytically determined C:W (or Mo) ratio and N:W (or Mo) ratios. The results are collected in Table 1.

Table 1
Protonation levels of HPA doped PIM used in catalytic tests as determined from elemental analysis

PIM structural unit: HPA molar ratio in the protonating medium	Protonation level determined per polyimine in the structural unit, i.e. $C_{14}H_{10}N_2$
$H_3PMo_{12}O_{40}$	
1:0.05	$PIM(HPA)_{0.008}$
1:0.10	$PIM(HPA)_{0.013}$
1:0.25	$PIM(HPA)_{0.066}$
1:1.00	$PIM(HPA)_{0.451}$
1:2.00	$PIM(HPA)_{0.708}$
$H_3PW_{12}O_{40}$	
1:0.05	$PIM(HPA)_{0.003}$
1:0.10	$PIM(HPA)_{0.038}$
1:0.25	$PIM(HPA)_{0.104}$
1:1.00	$PIM(HPA)_{0.468}$
1:2.00	$PIM(HPA)_{0.804}$
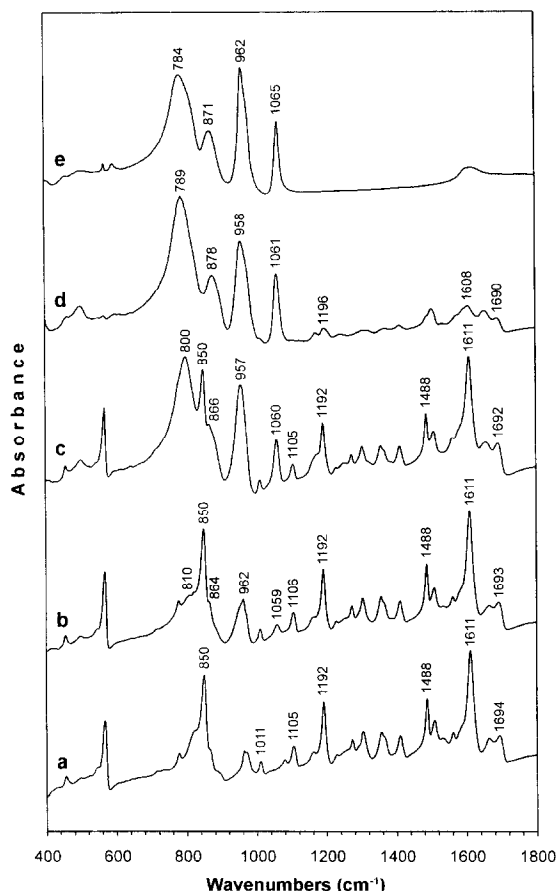
Fig. 1. FTIR spectra of: a: unprotonated PIM; b: $PIM(H_3PMo_{12}O_{40})_{0.013}$; c: $PIM(H_3PMo_{12}O_{40})_{0.066}$; d: $PIM(H_3PMo_{12}O_{40})_{0.451}$; e: crystalline $H_3PMo_{12}O_{40}$.

Protonation of PIM with heteropolyacids can also be conveniently monitored by FTIR spectroscopy. PIM in its basic, unprotonated form shows the presence of all IR bands expected for polyimine structures. In particular peaks characteristic of CH=N vibrations and para-substituted aromatic ring vibrations are present at 1611, 1105, 1080, 1011, and 850 cm^{-1} [20].

Protonation results in the appearance of the IR bands characteristic of the Keggin structural units which grow with increasing protonation level and at higher protonation levels totally dominate the spectrum (Figs. 1 and 2) [21].

It is interesting to note shifts in the positions of the IR bands originating from heteropolyanions vibrational modes when they are introduced into PIM matrix (Table 2). In particular in the case of PIM protonated with $H_3PMo_{12}O_{40}$ it concerns $\nu_{Mo-Oc-Mo}$ and $\nu_{Mo-Ob-Mo}$ bands which shift to higher and lower wavenumbers, respectively. In the case of PIM protonated with $H_3PW_{12}O_{40}$ at lower HPA contents one can observe a significant shift in the ν_{W-Oc-W} band to higher wavenumbers with respect to the spectrum of the crystalline heteropolyacid. Such changes in the band positions indicate some structural deformations of heteropolyanions
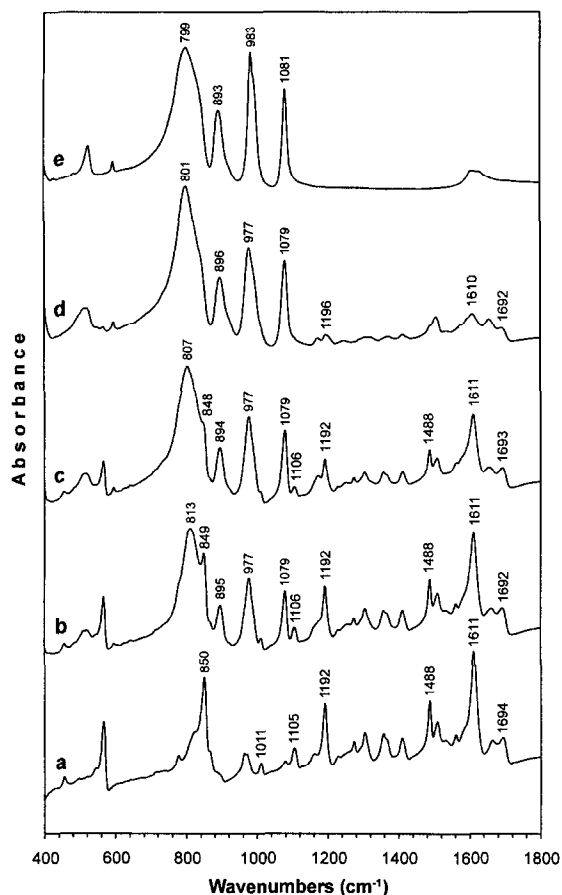
Fig. 2. FTIR spectra of: a: unprotonated PIM; b: PIM($H_3PW_{12}O_{40}$)$_{0.038}$; c: PIM($H_3PW_{12}O_{40}$)$_{0.104}$; d: PIM($H_3PW_{12}O_{40}$)$_{0.468}$; e: crystalline $H_3PW_{12}O_{40}$.

upon insertion to PIM matrix. In particular the shifts in ν_{M-Oc-M} (where M denotes W or Mo) bands suggest the deformation of structurally equivalent octahedra triple $[MO_6]_3$ subunit unit whereas the shift in ν_{M-Ob-M} band position indicates the changes in the relative locations of the adjacent octahedra in the Keggin unit structure.

These deformations of the Keggin structural units are inherently associated with the protonation reaction which results in strong ionic interactions between the polycations and the heteropolyanions. Similar phenomena have been observed in polyaniline protonated with heteropolyacids [22].

Here it should be noted, however, that in polyimine, for high heteropolyanion contents,

the IR band positions become again close to those observed for crystalline heteropolyacids (see Table 2). This means that the protonation is much more effective at low doping levels. At higher doping levels the acid molecules enter the polymer matrix but not necessarily all of them protonate the polyimine. For this reason the number of Brönsted acid centers increases with respect to the number of redox centers and the selectivity of the catalysts changes dramatically with increasing amounts of HPA (see Table 4).

Protonation of PIM with heteropolyacids causes broadening of the IR bands characteristic of the polymer matrix. This observation may suggest that the protonation reaction leads to significant amorphisation of the sample. We have therefore undertaken X-ray diffraction studies of unprotonated and protonated PIM.

Basic PIM is remarkably highly crystalline giving three distinct Bragg reflections at $d = 4.4$, 3.7 and 3.1 Å. High crystallinity of unprotonated polyimine is possibly associated with a rather oligomeric than polymeric nature of the samples prepared in this research. Kulszewicz-Bajer et al. [18], using a similar preparation method, obtained the product with the average polymerization degree equal to seven structural units, i.e. $(C_{14}H_{10}N_2)_7$. Increasing protonation results in a gradual disappearance of Bragg

Table 2
IR bands locations of the Keggin heteropolyanions for crystalline heteropolyacids and for PIM(HPA)$_y$

Sample	Band location (cm^{-1})			
	ν_{M-Oc-M}	ν_{M-Ob-M}	$\nu_{M=Od}$	ν_{X-Oa}
PIM($H_3PMo_{12}O_{40}$)$_{0.008}$	810	865	963	1059
PIM($H_3PMo_{12}O_{40}$)$_{0.013}$	810	864	962	1059
PIM($H_3PMo_{12}O_{40}$)$_{0.066}$	800	866	957	1060
PIM($H_3PMo_{12}O_{40}$)$_{0.451}$	789	878	958	1061
PIM($H_3PMo_{12}O_{40}$)$_{0.708}$	792	878	959	1061
Crystalline $H_3PMo_{12}O_{40}$	784	871	962	1065
PIM($H_3PW_{12}O_{40}$)$_{0.038}$	813	895	977	1079
PIM($H_3PW_{12}O_{40}$)$_{0.104}$	807	894	977	1079
PIM($H_3PW_{12}O_{40}$)$_{0.468}$	801	896	977	1079
PIM($H_3PW_{12}O_{40}$)$_{0.804}$	801	896	977	1079
Crystalline $H_3PW_{12}O_{40}$	799	893	983	1081
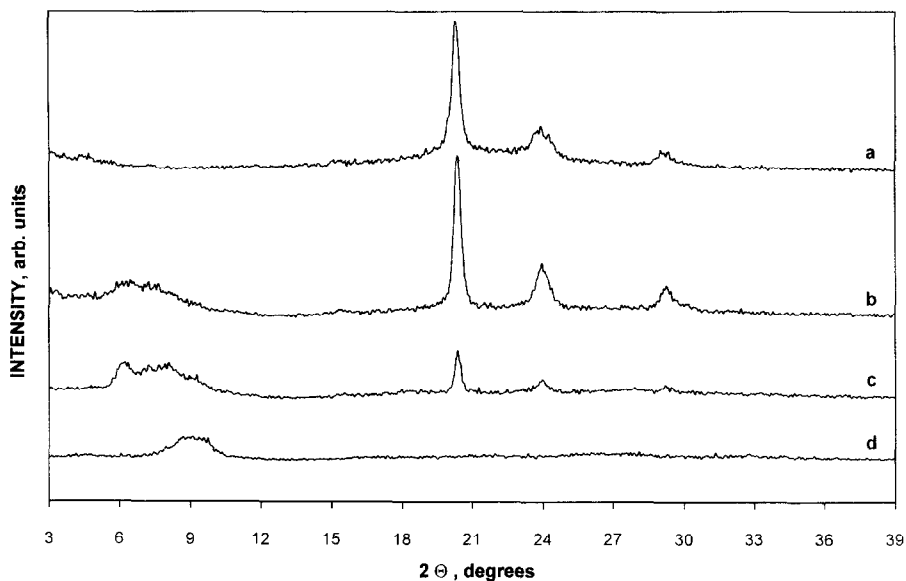
Fig. 3. X-ray diffraction patterns of: a: unprotonated PIM; b: PIM(H$_3$PMo$_{12}$O$_{40}$)$_{0.013}$; c: PIM(H$_3$PMo$_{12}$O$_{40}$)$_{0.066}$; d: PIM(H$_3$PMo$_{12}$O$_{40}$)$_{0.708}$. In the experiments Cu Kα radiation was used.

reflections characteristic of unprotonated crystalline phase with simultaneous appearance of a broad peak at $d \sim 9$–10 A (see Figs. 3 and 4). Very similar behavior has been observed by Hasik et al. [22] for HPA protonated polyaniline. The appearance of a new protonation-induced peak has been interpreted in terms of liquid-crystalline type ordering of heteropolyan-
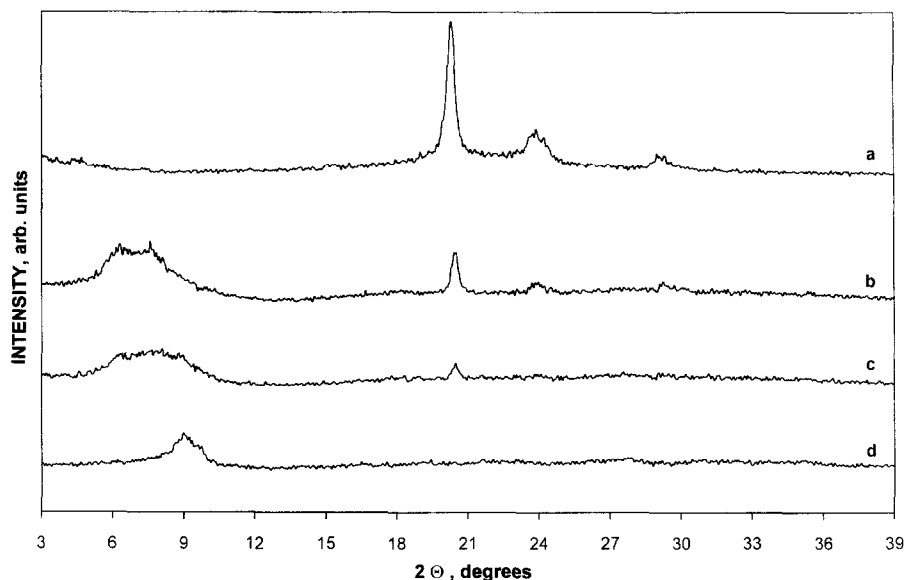

Fig. 4. X-ray diffraction patterns of: a: unprotonated PIM; b: PIM(H$_3$PW$_{12}$O$_{40}$)$_{0.038}$; c: PIM(H$_3$PW$_{12}$O$_{40}$)$_{0.104}$; d: PIM(H$_3$PW$_{12}$O$_{40}$)$_{0.804}$. In the experiments Cu Kα radiation was used.

ions in the polymer matrix. However, it is evident from the X-ray studies that the polymer matrix undergoes significant amorphisation.

Thermal stability of polymer supported heterogeneous catalyst is of crucial importance since several important catalytic processes are carried out at elevated temperatures. Basic (unprotonated) polyimine is remarkably thermally stable showing a two step decomposition with a small mass loss at 350°C and a strong mass loss at 470°C. PIM protonated with $H_3PW_{12}O_{40}$ also shows excellent thermal stability (Fig. 5). Small (1–2 wt%) mass loss observed at temperatures below 100°C is associated with removal of the adsorbed water which is always present in powdery samples. $H_3PMo_{12}O_{40}$ protonated PIM is less thermally stable, however, it does not show the decomposition at temperatures below 300°C. Of course thermogravimetry cannot be treated as a sole criterion of the sample thermal stability. The conclusions based on TG curves require spectroscopic verification of the preservation of the structural identity of the polymer after heat treatment. Such studies are in progress.

Catalytic conversion of isopropanol leads to two reaction products:

(1) on the acid–base centers propene is formed in the dehydration reaction:

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \longrightarrow CH_2 = CH - CH_3 + H_2O$$
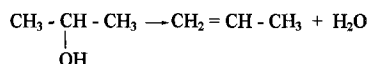
(2) on the redox centers acetone is formed according to the following reaction:

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \longrightarrow CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 + H_2$$
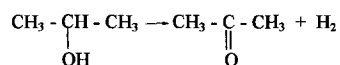
Crystalline heteropolyacids containing tungsten exhibit predominantly acid–base activity whereas in those containing molybdenum the redox activity is more enhanced.

Similarly as undoped polyaniline, undoped PIM is catalytically inactive. However, as in the case of polyaniline [17], the insertion of heteropolyacids into the PIM matrix via the protonation reaction significantly changes the selectivity as compared to unsupported HPA.

Since selectivity can be calculated in a number of ways, for clarity of this paper we include its definition which constitutes the basis for the calculation of the selectivity used in this re-
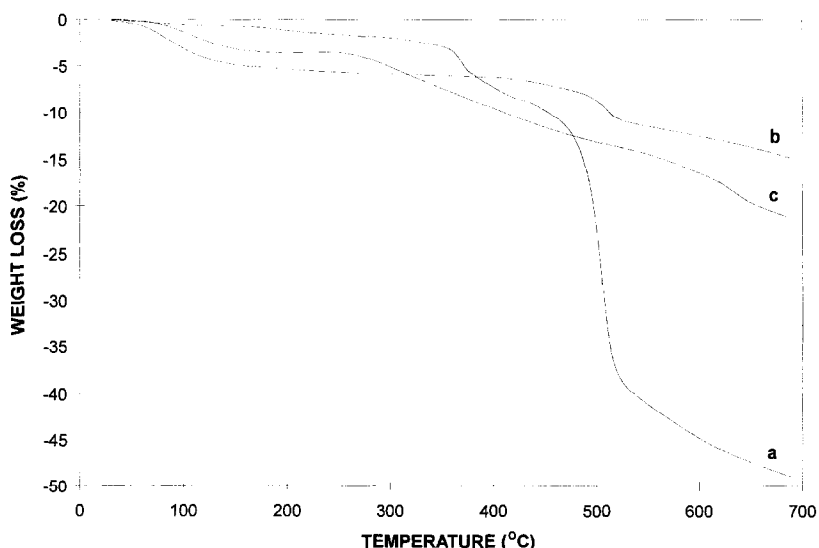

Fig. 5. Thermogravimeric curves for: a: undoped PIM; b: $PIM(H_3PW_{12}O_{40})_{0.804}$; c: $PIM(H_3PMo_{12}O_{40})_{0.708}$.

Table 3
Selectivities and activation energies of the catalytic isopropanol conversion measured for PIM and polyaniline protonated with $H_3PW_{12}O_{40}$

Sample composition	HPA content in the sample (wt%)	Selectivity at 406 K (%)		Activation energy (kJ/mol)	
		propene	acetone	dehydration	dehydrogenation
$PIM(H_3PW_{12}O_{40})_{0.038}$	34.7	4.0	96.0	96.4	43.8
$PANI(H_3PW_{12}O_{40})_{0.018}^a$	35.2	3.1	96.9	136.2	69.4

[a] Data taken from Ref. [17].

search. Thus selectivity to a given product is calculated as the number of moles of the substrate (isopropanol) used for the formation of this product divided by the number of moles of the substrate used for the formation of all products in all parallel reactions occurring in the system.

PIM protonated with $H_3PW_{12}O_{40}$ at low protonation levels shows extremely high selectivity towards acetone at 406 K which for the sample $PIM(H_3PW_{12}O_{40})_{0.038}$ is equal to 96%.

It is interesting to compare catalytic properties of $PIM-H_3PW_{12}O_{40}$ system with polyaniline–$H_3PW_{12}O_{40}$ containing the same amount of heteropolyacid and studied in the same experimental conditions. The results are summarized in Table 3.

It is striking that the selectivity results obtained for polyaniline and polyimine doped with the same amounts of heteropolyacids, are very similar. This observation is a simple consequence of the same type of reactions occurring in both system, i.e. the protonation of imine sites by heteropolyacid molecules inserted to the polymer matrix. Since upon protonation of the polymer chain the heteropolyacid molecule is transformed into a weak base a decrease in the

number of acidic sites is expected and the catalyst shows predominantly redox activity with high selectivity towards acetone.

However, with increasing HPA content in polyimine the selectivity towards acetone formation decreases (Table 4). This result strongly corroborates the results of FTIR spectroscopy which indicate that with increasing amount of heteropolyacid molecules inserted to the polymer matrix the efficiency of the protonation of the polymer chain decreases.

Quantitatively the same results are obtained for $PIM(H_3PMo_{12}O_{40})_y$, i.e. the selectivity towards acetone decreases with increasing heteropolyacid content in the polymer matrix (Table 5).

However, two differences between $PIM(H_3PW_{12}O_{40})_y$ and $PIM(H_3PMo_{12}O_{40})_y$ must be pointed out:

(1) in general $PIM(H_3PMo_{12}O_{40})_y$ shows higher catalytic activity in isopropanol conversion;

(2) the selectivity towards acetone formation is not so high for $PIM(H_3PMo_{12}O_{40})_y$ at low contents of HPA as it is for $PIM(H_3PW_{12}O_{40})_y$. This means that $H_3PMo_{12}O_{40}$ is a less efficient protonating agent than $H_3PW_{12}O_{40}$.

In Figs. 6 and 7, Arrhenius plots for

Table 4
Selectivities of $PIM(H_3PW_{12}O_{40})_y$ catalysts in isopropanol conversion

Sample composition	HPA content in the sample (wt%)	Selectivity at 406 K	
		propene	acetone
$PIM(H_3PW_{12}O_{40})_{0.038}$	34.7	4.0	96.0
$PIM(H_3PW_{12}O_{40})_{0.104}$	59.2	12.1	87.9
$PIM(H_3PW_{12}O_{40})_{0.468}$	86.7	89.5	10.5
$PIM(H_3PW_{12}O_{40})_{0.804}$	91.8	96.9	3.1

Table 5
Selectivities of $PIM(H_3PMo_{12}O_{40})_y$ catalysts in isopropanol conversion

Sample composition	HPA content in the sample (wt%)	Selectivity at 406 K	
		propene	acetone
$PIM(H_3PMo_{12}O_{40})_{0.013}$	10.5	23.2	76.8
$PIM(H_3PMo_{12}O_{40})_{0.066}$	36.9	52.0	48.0
$PIM(H_3PMo_{12}O_{40})_{0.451}$	79.9	72.2	27.8
$PIM(H_3PMo_{12}O_{40})_{0.708}$	86.2	90.2	9.8

PIM ($H_3PW_{12}O_{40}$)$_{0.038}$ and PIM($H_3PMo_{12}O_{40}$)$_{0.066}$ are presented. At higher temperatures, significant curvatures are observed for faster reactions (curve 2 in Fig. 6 and curve 1 in Fig. 7). These changes in the slope can be interpreted as the transition from the kinetic limit of the reaction to the diffusion limit.

Finally it should be pointed out that the reaction of PIM doping with heteropolyacids is a solid state reaction in which the polymer matrix remains solid in the course of the doping process. Taking into account the size of heteropolyanions the diffusion of the dopant may be limited to close to the surface area. If this is the case a strong dependence of the protonation
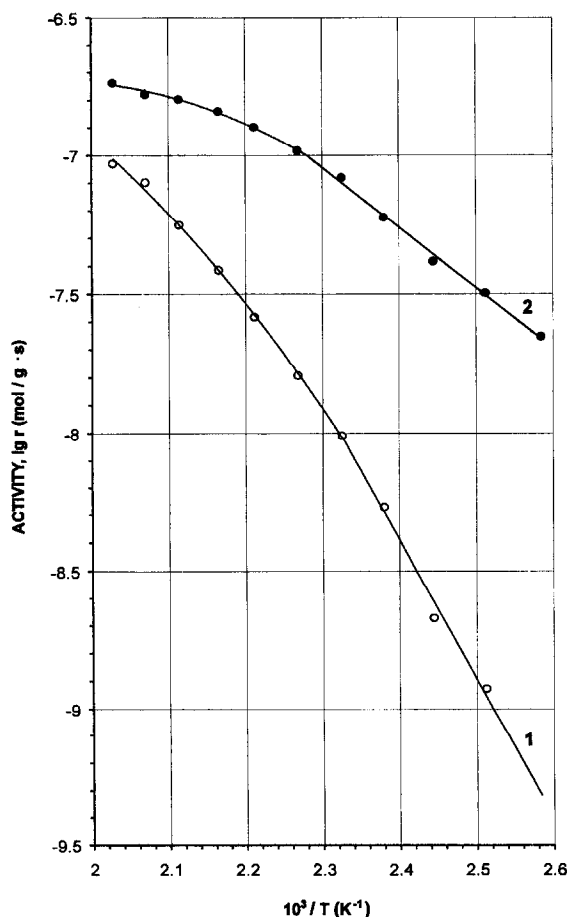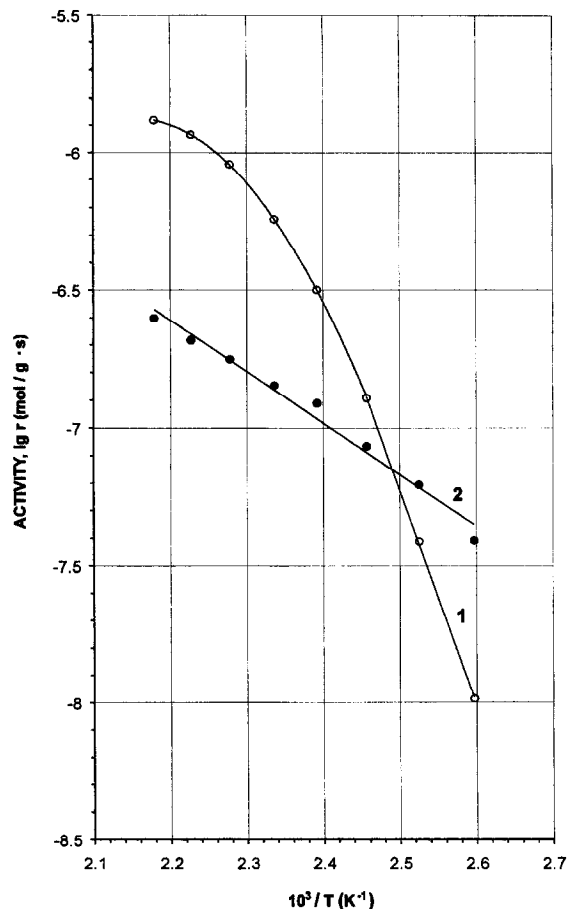

Fig. 7. Arrhenius plots of isopropanol decomposition over PIM($H_3PMo_{12}O_{40}$)$_{0.066}$. (1) Propylene; (2) acetone.

efficiency on the specific surface of the polymer is expected. Studies of the protonation of PIM samples differing in the specific surface area are in progress.

4. Conclusions

To summarize we have shown that heteropolyanions of the Keggin-type can be inserted to poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) via protonation at the basic sites of the polymer with heteropolyacids, similarly as in the case of polyaniline. This protonation assisted introduction of heteropolyacids into the polymer matrix

Fig. 6. Arrhenius plots of isopropanol decomposition over PIM($H_3PW_{12}O_{40}$)$_{0.038}$. (1) Propylene; (2) acetone.

effectively blocks acid–base functions for low contents of heteropolyacids. As a result poly-imine supported catalysts with low heteropoly-acids content exhibit predominantly redox activity and very high selectivity towards acetone formation.

Acknowledgements

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