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# Synthesis and characterizations of new negatively charged organic–inorganic hybrid materials: effect of molecular weight of sol–gel precursor

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**Abstract**

A series of negatively charged hybrid (organic–inorganic) materials were prepared through sol–gel process. The alkoxysilane-containing sol–gel precursors PEO-$[Si(OEt)_3]_2SO_3H$ were obtained by endcapping polyethylene oxide (PEO) of different molecular weights with 2,4-diisocyanate toluene (TDI), followed by a coupling reaction with phenylaminomethyl triethoxysilane (ND-42) and sulfonation afterwards. The negatively charged precursors were then hydrolyzed and condensed to generate hybrid sol–gel materials, which were characterized by IR, TGA, XRD as well as the conventional ion exchange measurements. The results showed that in the hybrid sol–gel precursors PEO-$[Si(OEt)_3]_2SO_3H$ organic PEO component was incorporated with alkoxysilane-containing ND-42 covalently. As the molecular weight of the precursors increased, thermal stability and cation-exchange capacity of the hybrid material decreased. All the hybrid materials were amorphous and those prepared from higher molecular weight precursors were flexible.

*Keywords:* Negatively charged materials; Organic–inorganic hybrid materials; Sol–gel; Sulfonation

## 1. Introduction

Sol–gel derived organic–inorganic hybrid materials have received a great amount of scientific and technological interests during the past two decades [1–7]. The ambient processing condition of the sol–gel technique could be adapted to construct nanocomposites of both organic and inorganic components. To disperse inorganic oxides, such as silica, uniformly in organic matrix, weak interactions (hydrogen bonding, aromatic interactions, ionic interaction, and so on) or covalent bond would be formed between organic components and silica. Usually covalent bond would result in a more homogeneous system.

Among the many varieties of organic–inorganic materials explored up to now, charged ones have recently received particular attention in such fields as battery, electrochromic windows, displays, low and medium temperature fuel cells, etc., since this kind of hybrid materials can associate the mechanical and thermal resistance of the silica backbone with the flexibility and conductivity of the organic components [8–11]. Especially, charged hybrid materials have also been found important in liquid separation membrane fields such as ultrafiltration or nanofiltration, due to their combined advantages over both inorganic membranes and polymeric membranes [12,13].

For the preparation of charged hybrid materials, the conventional method is through the hydrolysis and condensation reaction of alkoxysilanes possessing negatively or positively charged organic residues. On some occasions, non-charged, yet reactive polymerizable alkoxysilanes were also added into the sol–gel reaction system, so that thermal or uv-initiated polymerization reaction could take place following the sol–gel process to obtain more stable and insoluble hybrid materials [8,10]. However, currently, the frequently used sol–gel precursors are alkoxysilanes of relatively low molecular weight, therefore, it is hard to obtain hybrid materials with high organic component and thus the flexibility of the obtained hybrid materials is quite limited and show disadvantages in the above application fields.

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To obtain hybrid materials with high organic component (and thus high flexibility), a negatively charged hybrid sol–gel precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H with relatively high molecular weight is to be initiated in this paper and the corresponding new negatively charged organic–inorganic hybrid material synthesized by hydrolysis and condensation reactions of the precursor. The effect of the molecular weight of polyethylene oxide (PEO) on the properties of the hybrid materials will be fully explored by FTIR spectra, thermal analysis, XRD analysis as well as ion-exchange measurements.

## 2. Experiment

### 2.1. Materials

Phenylaminomethyl triethoxysilane (ND-42) and 2,4-diisocyanate toluene (TDI) were purchased from a domestic chemical reagent company and were purified by distillation before use. PEO (molecular weight = 200, 400, 600, 800, 1000) and dimethyl formamide (DMF) were carefully got rid of water before use (PEO through drying at 100°C at 2 mmHg and DMF through molecular sieve drying). Other reagents were used as received.

### 2.2. Preparation of negatively charged sol–gel precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H

Into a three-necked round-bottom flask, which was equipped with a stirrer, an N$_2$ inlet and a cooler/heater, TDI dissolved in proper amount of dimethyl formamide (DMF) was added. Then a stoichiometric amount of PEO (PEO:TDI = 1:2, molar ratio) was dropped into the flask within 40 min. The solution was heated at 30°C and stirred for additional 20 h. Then, into the resultant product–colorless endcapped PEO, stoichiometric amounts of ND-42 (TDT:ND-42 = 1:1,molar ratio) was added and stirred at 60°C for additional 6 h. At the end of the reaction, ethanol was added to precipitate the product. The pure reaction product PEO-[Si(OEt)$_3$]$_2$ was obtained by washing with ethanol for several times and then drying at 50°C under vaccum (5 mmHg).

In a three-necked round-bottom flask, with the same equipment as described above, the pure product PEO-[Si(OEt)$_3$]$_2$ was dissolved in DMF. Excessive fuming sulfuric acid (20% SO$_3$) (acid: PEO-[Si(OEt)$_3$]$_2$ = 6:1, molar ratio) was dropped slowly into the solution. The mixture was stirred for 12 h at temperatures lower than 20°C. Finally the mixture was precipitated and washed with isopropanol, vacuum-dried at 50°C to get the sol–gel precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H.

### 2.3. Preparation of the organic–inorganic hybrid materials

The synthesized precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H was dissolved in DMF at 70°C to get a 10% (w/w) solution. Then water and 0.1 M HCl (PEO-[Si(OEt)$_3$]$_2$SO$_3$H : H$_2$O : HCl = 1 : 10 : 0.001, molar ratio) were added while violently stirred. The mixture was stirred at 60°C for 30 min, and then dropped onto Teflon plate. After drying at room temperature for one day, the plate was heated from 50°C to 100°C and kept at 100°C for three hours. After removal from the plate, the final hybrid material was obtained. The hybrid material prepared from PEO 200, 400, 600, 800, 1000 was denoted as hybrid A, B, C, D and E, repectively. All were flexible except hybrid A.

Some composite films were prepared for XRD observations by spin-coating the solution (after 30 min of stirring at 60°C) onto a silicon slice ($1\,\mathrm{cm} \times 1\,\mathrm{cm} \times 0.05\,\mathrm{cm}$), followed by the same drying and heating procedure as mentioned above.

### 2.4. Characterizations

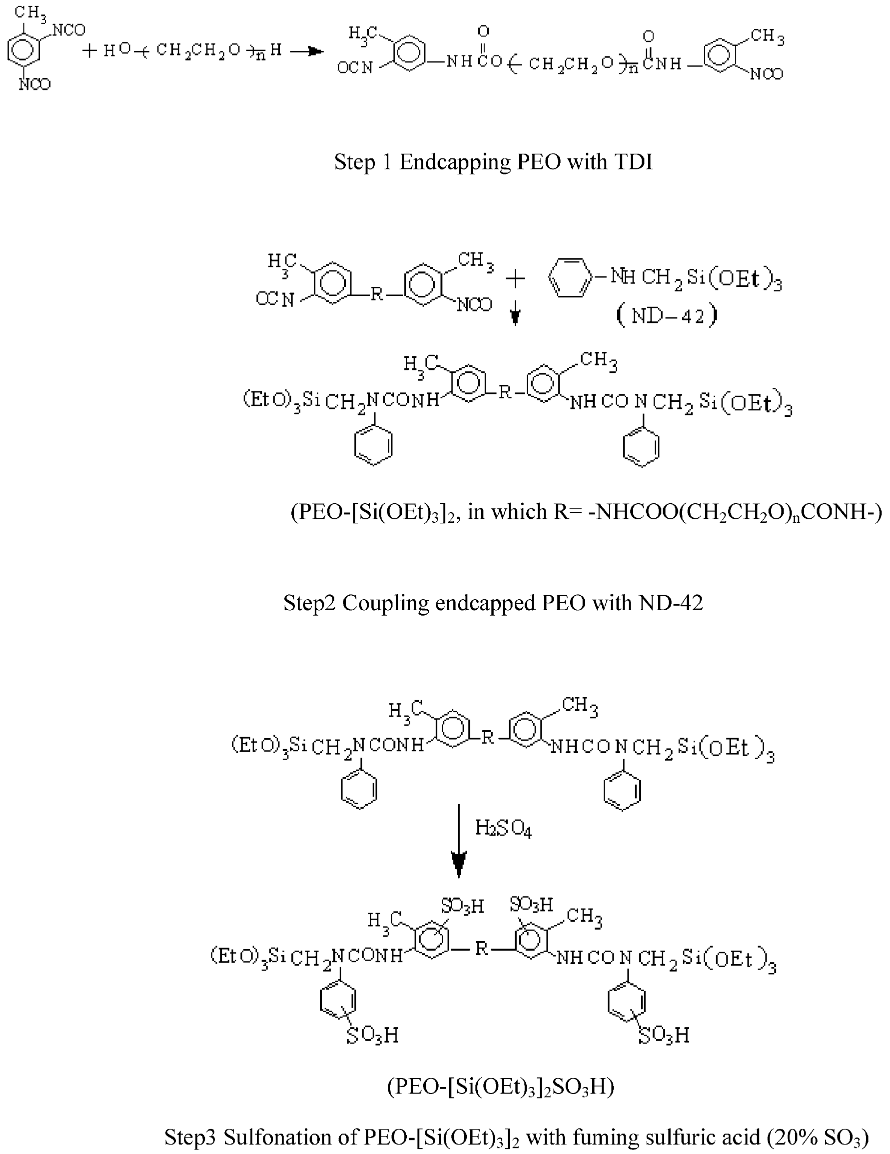
The characterizations include: FTIR spectra, the ionic exchange capacity, crystallinity and thermal stability of the hybrid materials and/or the step products, etc. FTIR spectra of the step products endcapped PEO, PEO-[Si(OEt)$_3$]$_2$, PEO-[Si(OEt)$_3$]$_2$SO$_3$H, and the hybrid materials were recorded with a Magna-750 FTIR (American Nicolet Instrument Co.). The thermal behavior of the hybrid materials was determined with thermogravimetry analyzer under a N$_2$ flow, with the heating rate of 10°C/min. The cation-exchange capacities (IEC) of the hybrid materials were determined by the conventional method [14], in which the hybrid materials in their H$^+$ ionic form were neutralized with NaOH, then back titrated with 0.01 M HCl. From the obtained IEC values, sulfonation degree of the hybrid material could be calculated assuming complete conversion of Si(OEt) groups in PEO-[Si(OEt)$_3$]$_2$SO$_3$H to Si–O–Si groups after the sol–gel process.

Crystallinity of the hybrid materials was conducted by the X-ray diffraction (XRD) technique, using Cu$K\alpha$ ($\lambda = 1.54178$ Å) radiation on a Japan Rigaku D/max-$\gamma$A X-ray diffractometer.

## 3. Results and discussion

### 3.1. Synthesis of the negatively charged sol–gel precursor

As mentioned in the experimental section, synthesis of the negatively charged sol–gel precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H includes three steps. The possible step reactions are shown in Scheme 1.



Step 1 Endcapping PEO with TDI

(PEO-[Si(OEt)$_3$]$_2$, in which R= -NHCOO(CH$_2$CH$_2$O)$_n$CONH-)

Step2 Coupling endcapped PEO with ND-42

(PEO-[Si(OEt)$_3$]$_2$SO$_3$H)

Step3 Sulfonation of PEO-[Si(OEt)$_3$]$_2$ with fuming sulfuric acid (20% SO$_3$)

Scheme 1. The step reactions for preparing precursor PEO-[Si(OEt)$_3$]$_2$SO$_3$H.

Step 1 is a hydrogen shift reaction between TDI and PEO, resulting in urethane coupling between their molecules. Endcapped PEO is the product of this step. Since the molar ratio between TDI and PEO is 2:1, therefore, mainly the 4-isocyanate (–NCO) group on TDI molecules takes part in the reaction, with the 2-isocyanate group remaining unreacted. Step 2 is a coupling reaction of ND-42 with the endcapped PEO. In this reaction, –NH– groups of ND-42 react with the remaining –NCO groups of endcapped PEO, forming urea linkage. The product of this step, PEO-[Si(OEt)$_3$]$_2$, contains phenyl groups on its molecule, so it can undergo the following sulfonation reaction (step 3). It should be noted that during step 3, the reaction temperature should be controlled lower than 20°C due to the temperature limitation of the urethane groups under high acidic conditions. In addition, to avoid the cleavage of the urethane groups, relatively mild sulfonation agent, fuming sulfuric acid (20% SO$_3$), was used instead of chlorosulfonic acid.

To confirm the above reactions, products from PEO 400 in the three steps were characterized with FTIR for an example. Fig. 1 shows the FTIR spectra of (a) endcapped PEO 400; (b) PEO-[Si(OEt)$_3$]$_2$ and (c) PEO-[Si(OEt)$_3$]$_2$SO$_3$H. In (a), a distinct absorption peak at $\sim 1100\,\text{cm}^{-1}$ is in the region of $-\text{C}-\text{O}-\text{C}$ stretching for ether groups and the peak at $\sim 2270\,\text{cm}^{-1}$ confirms the existence of $-\text{NCO}$ groups. The characteristic bands of urethane groups are observed at $\sim 3260\,\text{cm}^{-1}$ ($\nu_{\text{NH}}$) and $\sim 1720\,\text{cm}^{-1}$ ($\nu_{\text{C=O}}$). In (b), the peak at $\sim 2270\,\text{cm}^{-1}$ disappears, while the peak at $\sim 1100\,\text{cm}^{-1}$ increases since the Si–O–C stretching from ethoxysilane groups is in this region and overlaps with –C–O–C stretching band. These changes compared with Fig. 1(a) approved

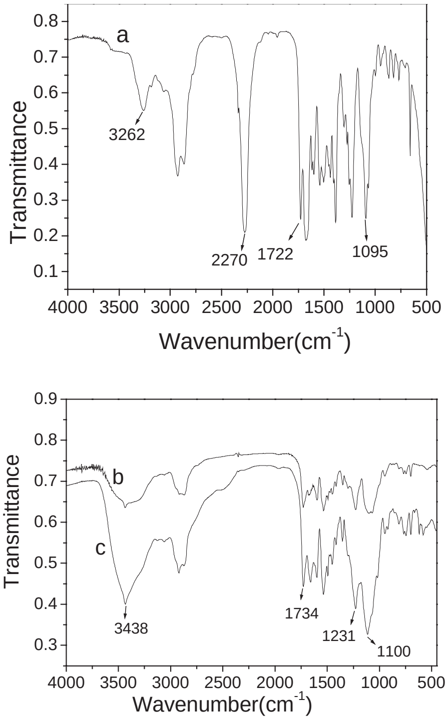


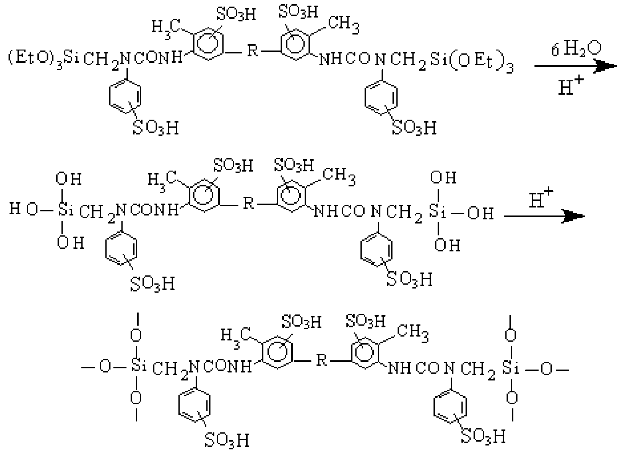
Fig. 1. The FTIR spectra of (a) endcapped PEO-400 (b) PEO-$[Si(OEt)_3]_2$ and (c) PEO-$[Si(OEt)_3]_2SO_3H$.

that organic PEO component was incorporated with ND-42 covalently. Fig. 1(c) is very close to Fig. 1(b), except for the increasing of the bands at $\sim$1100, 1230 and 3440 cm$^{-1}$. This increasing can be easily explained since characteristic peaks of –$SO_3H$ groups in PEO-$[Si(OEt)_3]_2SO_3H$ are in the region $\sim$1100 ($\nu_{s\ SO_2}$), $\sim$1200 cm$^{-1}$ ($\nu_{as\ SO_2}$) and $\sim$3400 cm$^{-1}$ ($\nu_{-OH}$). The ion-exchange capacity (IEC) discussed in the following section will conform further formation of –$SO_3^-H^+$ groups during the sulfonation process (step 3 in Scheme 1).

### 3.2. FTIR spectra and thermal stability of the hybrid materials

The hybrid materials were prepared via the sol–gel process. To identify more clearly their chemical structure and thermal stability, the precursors PEO-$[Si(OEt)_3]_2SO_3H$ were directly hydrolyzed and condensed with a trace of HCl aqueous solution (as shown in Scheme 2) without adding any coupling agent, such as tetraethoxysilane or tetramethoxysilane.

Fig. 2 shows the FTIR spectra of the five hybrid materials A, B, C, D and E after heat treatment. Absorption bands at $\sim$1100 cm$^{-1}$ are all quite strong in Fig. 3 and should include the newly formed Si–O–Si stretching during the sol–gel process. However, it seems that there is no considerable change in the intensity of this absorption band when the hybrid materials (Fig. 2) and the sol–gel precursor PEO-$[Si(OEt)_3]_2SO_3H$ (Fig. 1(c)) are compared. This is possibly due to the complexity of the spectra: $\nu_{Si-O-Si}$, $\nu_{Si-O-C}$, $\nu_{C-O-C}$ and ($\nu_{s\ SO_2}$) which are all in the region of 1050–1150 cm$^{-1}$, so that the contribution of newly formed Si–O–Si groups cannot be well identified. Also due to the complexity of the spectra, differences in the intensities of inorganic Si–O–Si bands and organic C–O–C bands among the different hybrid materials A, B, C, D, and E (Fig. 2) cannot be clearly distinguished.



Scheme 2. Hydrolysis and polycondensation reactions of PEO-$[Si(OEt)_3]_2SO_3H$ to form organic–inorganic hybrid materials.

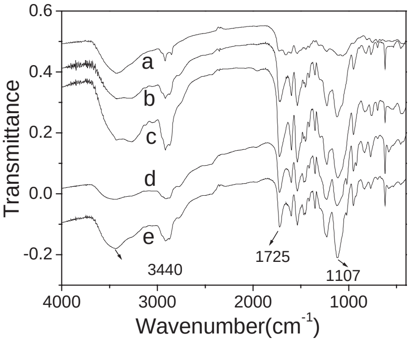


Fig. 2. The FTIR spectrum of the hybrid (a) A; (b) B; (c) C; (d) D and (e) E.

To identify these differences and check the thermal stabilities of the hybrid materials, thermogravimetry analyses (TGA) were produced and the results are shown in Fig. 3(a). TGA thermogram (Fig. 3(a)) can be used to determine both the inorganic silica contents (which are evaluated from the residual weight at 800°C) and $T_d$'s (defined as the temperature at 5% weight loss). The residual $SiO_2$ contents and the $T_d$'s for five hybrid materials determined from TGA in such a manner are collected in Table 1. Obviously, both silica content and $T_d$ of the hybrid material decrease with an increase of PEO molecular weight. This result coincides with the fact that the thermal stability of the hybrid material decreases with a decrease in the inorganic silica content [15].

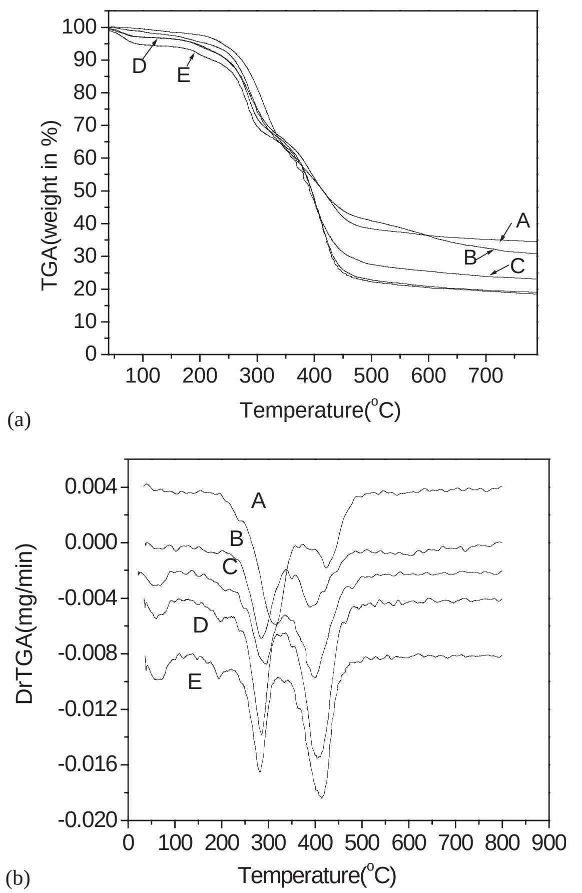


Fig. 3. (a) TGA and (b) DrTGA results for the hybrid (a) A; (b) B; (c) C; (d) D and (e) E.

Table 1
Thermal properties and residual $SiO_2$ content of hybrid materials prepared from PEO with different molecular weights

| Hybrid | A | B | C | D | E |
|---|---|---|---|---|---|
| Residual $SiO_2$ contents (wt%)[a] | 34.42 | 30.82 | 22.85 | 18.91 | 18.30 |
| $T_d$ (°C)[b] | 239 | 212 | 193 | 191 | 158 |

[a] Residual $SiO_2$ contents are obtained from TGA thermograms, which were performed at a heating rate 10°C/min under $N_2$ atmosphere.

[b] The thermal degradation temperatures ($T_d$) are defined as weight loss of TGA thermogram at 5 wt%.

Further observation of the hybrid materials' TGA thermograms (Fig. 3(a)) reveals that the thermal degradation behaviors of the hybrid materials are divided into two stages. To show these stages more clearly, DrTGA results of the hybrid materials are displayed in Fig. 3(b). It can be seen that for all the hybrid materials the first weight loss peak is at around 300°C, while the second is at around 400°C. Consulting the thermogravimetric observations of hybrid materials containing similar components [3,16], the first degradation stage of our hybrid materials may be caused by the cleavage of relatively unstable groups such as the urethane and the sulfonic groups, whereas the second stage is due to the degradation of the PEO component. The data suggest that the thermal stability of the polymer PEO phase in the hybrids is highly enhanced by the nanolevel confinement in the inorganic $SiO_2$ framework. Another point is that organic PEO content in the hybrid material increases in the order of A–E, thus the intensity of the second weight-loss peak increases correspondingly as indicated in Fig. 3(b).

### *3.3. Ion-exchange capacity*

To find the influence of PEO molecular weights on the IEC of the hybrid materials, IEC measurements of the five kinds of hybrid materials were conducted and the results are shown in Table 2. As can be seen, the cation-exchange capacities of the prepared hybrid materials decrease with the PEO molecular weight in the range of 0.3–1.5 meq/g. The possible reasons may be (i) the sulfonation process: when the PEO molecular weight increases, both the steric hindrance of the phenyl groups and the viscosity of the reaction system increase to some degree, and thus the sulfonation reaction becomes more difficult and the sulfonation degree decreases, as shown in Table 2; (ii) the molecular weight of the hybrid materials increases with the PEO molecular weight and this leads to a decrease in ion exchange capacity.

Formation of negatively charged groups in the hybrid materials may be explained by the reaction Scheme 1 mentioned above: since the product of step 2 in Scheme 1, PEO-$[Si(OEt)_3]_2$, possesses phenyl groups, it can undergo conventional sulfonation reaction as described by step 3 of Scheme 1. We have attempted to determine the exact position of sulfonic groups through NMR spectra, but failed. Due to the phenyl groups' quite low density and the complexity of the substituents on the phenyl groups, the obtained NMR cannot permit a precise determination of the sulfonic groups' position. However, this seems less important in our work because our only concern is the negative charge characteristics which depend on the sulfonic groups not on the position.

Table 2
Cation-exchange capacities and sulfonation degree of the hybrid materials prepared from PEO with different molecular weights

| Hybrid | A | B | C | D | E |
|---|---|---|---|---|---|
| IEC (mmol/g) | 1.473 | 1.151 | 0.666 | 0.415 | 0.304 |
| Sulfonation degree | 0.52 | 0.46 | 0.30 | 0.21 | 0.17 |

### 3.4. X-ray diffraction

XRD measurements were conducted to estimate the crystallinity of the hybrid materials and the results are shown in Fig. 4. Since hybrid A was very brittle, it was ground into fine powder for the X-ray measurement, while for hybrid B–E, diffractograms were taken from films on silicon substrates. It seems that there are no obvious differences in the diffractograms of B–E, so only those of the hybrid material B and D are shown here as the examples.

In Fig. 4(a), a diffractogram typical of amorphous samples can be seen, while in Figs. 4(b) and (c), no peaks of crystallinity except that of the silicon substrate are observed. So all the hybrid materials prepared are amorphous, despite the difference in their PEO content. Our results differ from those reported by Sforca et al. [17], in which organic–inorganic hybrid film composed of polyether and silica components shows higher crystallinity as the polyether increased from $M_w = 900$ to 2000. The reasons may be that: (a) in Ref. [17], poly (propylene glycol)-*block*-poly (ethylene glycol)-*block*-poly (propylene glycol) bis (2-aminepropyl ether) (PAPE) was used as the organic composition and PAPE showed higher tendency to crystallize than PEO; (b) in our work, the molecular weights' range of PEO (200–1000) used in the hybrid materials' preparation is smaller than that of PAPE (900–2000) used in the literature.

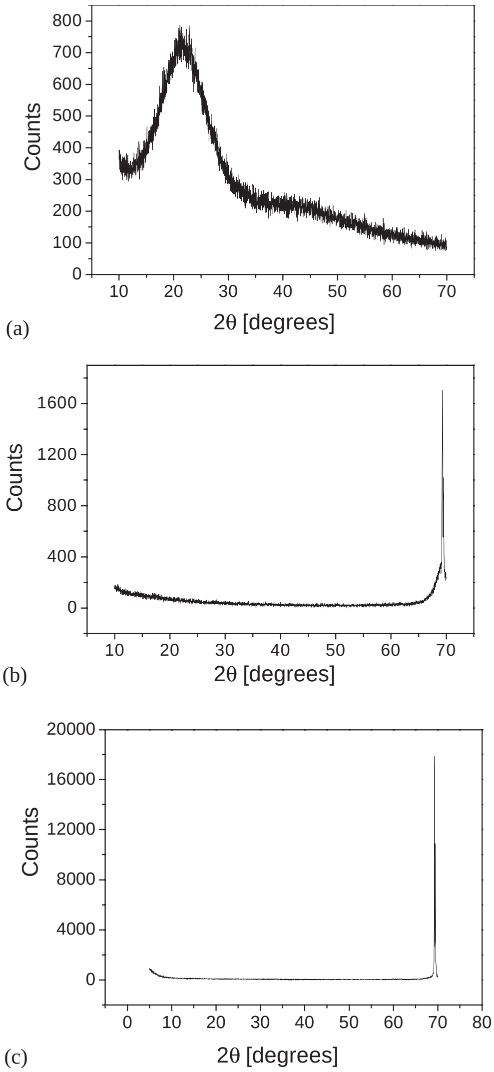


Fig. 4. X-ray diffractograms of the hybrid (a) A; (b) B and (c) D.

## 4. Conclusions

New organic–inorganic precursor PEO-$[Si(OEt)_3]_2$ $SO_3H$ was synthesized by coupling ND-42 to endcapped PEO of different molecular weights, followed by sulfonation reaction. Based on this precursor, a series of negatively charged hybrid materials were prepared by sol–gel process. The hybrid materials were conducted FITR, TGA, IEC as well as XRD measurements. FTIR results revealed that during the preparation of negatively charged sol–gel precursor, PEO component was incorporated with alkoxysilane-containing ND-42 covalently. From TGA, it was observed that both silica content and $T_d$ of the hybrid material decreased with an increase of PEO molecular weight. Another interesting point was that the thermal degradation behaviors of the hybrid materials were clearly divided into two stages. As the molecular weight of PEO increased, intensity of the second weight-loss peak at around 400°C which is due to the degradation behavior of PEO component increased.

As the molecular weight of PEO increased, IEC values of the hybrid materials decreased from 1.5 (hybrid A from PEO 200) to 0.3 meq/g (hybrid E from PEO 1000), due to both the decreasing of the sulfonation degree and the increasing of the hybrid's molecular weight. XRD measurements showed that all the hybrid materials prepared were amorphous.

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