

The role of crystalline phase in triblock copolymer PS–PEG–PS based gas sensing materials

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Abstract

To reveal the role of crystalline phase in the matrix polymer of gas sensing conductive polymer composite materials, a series of triblock copolymer polystyrene-*b*-poly(ethylene glycol)-*b*-polystyrene (PS–PEG–PS) was synthesized by atom transfer radical polymerization (ATRP). The copolymers have similar molecular weights but different fractions of the crystalline PEG segments. As a result, the ratio of the crystalline phase to the amorphous one can be tuned regardless of the molecular weight of the entire copolymer. The composites consisting of the copolymer and carbon black exhibit gas sensing ability as characterized by the drastic increase in the electrical resistance when meeting organic solvent vapors. It is found that matrix swelling, which provides the composites with gas sensitivity, results from the contribution of the amorphous phase. The crystalline portions prove to be unchanged in the vapors with respect to their microstructure within the time of interests. The appearance of the crystalline phase in the matrix polymer helps to push the conductive fillers into the amorphous regions, which increases the effective filler content and leads to higher responsiveness to solvent vapors at lower filler loading.

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1. Introduction

Intrinsically insulating polymers might acquire conductivity by blending with conductive fillers [1]. Recently, the gas sensibility of these conducting composite materials has received increasing attention as they have brilliant prospects in chemical, medical, automotive, package, food, beverage, fragrance and environmental fields to detect, quantify and discriminate various organic vapors [2–11]. Compared with the sensors made from intrinsically conducting polymers or inorganic oxides, the ones based on conductive polymer composites possess higher sensitivity, better processability and cost effectiveness [12]. The functional mechanism is generally interpreted as the following processes. Upon exposure to an odorant, the composite materials will swell to some degrees depending on the polymer-odorant interactions. It is believed that this swelling results in redistribution of the conductive fillers in the matrix and hence a change in the resistance of

composites, which provides measurable signals characterizing the surrounding vapor-phase analytes.

With respect to the polymers used in these materials, which is one of the interesting topics for materials scientists, it is found that crystalline polymers are in the majority as viewed from the available literature. This is because the researchers suggest that crystallinity of the matrix polymer exerts important influence on the gas responsiveness, and the crystalline phases would be partially dissolved by the absorbed solvent vapors, accounting for the reversible destruction of the conductive networks [13]. Tsubokawa and co-workers, for example, showed that the electric resistance of the composites from polymer-grafted carbon black and crystalline polymers increases by several orders of magnitude in some solvent vapors [2–5]. It was concluded that the significant responsiveness resulted from breakdown of conducting networks in the composites driven by the dissolved crystalline phases during absorption of the solvent vapors. However, the experiments in our laboratory demonstrated that the amorphous polymer-based composites also exhibited high sensitivity to many solvent vapors [14–17]. Evidently, the results come into conflict with the aforesaid consideration. It means that swelling or dissolve of the amorphous phase itself of a polymer matrix

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might be sufficient to bring in the remarkable variation in resistance of the composites exposed to solvent vapors. In this context, whether the transformation of crystalline phases of a crystalline polymer matrix into amorphous ones is the controlling mechanism involved in the gas sensibility of the composites becomes questionable.

To reveal the role of crystalline phases in crystalline polymers based gas sensing composites, a series of triblock copolymer of polystyrene-*b*-poly(ethylene glycol)-*b*-polystyrene (PS-PEG-PS) containing both crystalline segments poly(ethylene glycol) (PEG) and amorphous polystyrene (PS) are synthesized by atom transfer radical polymerization (ATRP) [18–20] and then compounded with conductive fillers in this work. The molecular weight and the fractions of PEG segments in the resultant copolymers are purposely designed to evaluate the effect of the crystalline phase on the gas sensibility of the corresponding composite materials. It is expected that the outcomes of the present study would also be helpful for materials selection when constructing gas sensing polymer composites.

2. Experimental works

2.1. Materials

Carbon black (XC-72) purchased from Cabot Co. Ltd (specific surface area: 254 m²/g, DBP value: 174 ml/100 g, average particle size: 50–70 nm) was dried at 110 °C in vacuum for 48 h before use. 4,4'-Azobis(4-cyanovaleric acid) (ACPA, Acros Organics, 97%) and *N,N'*-dicyclohexylcarbodiimide (DCC, Songjiang Chahua Adhesive Factory, Shanghai, China, A.R.) were used as received.

Styrene was successively washed with 5% aqueous NaOH and H₂O, dried by CaCl₂ and then distilled under reduced pressure before use. CuCl was washed with HAc and acetone, respectively, and then dried at 60 °C in vacuum for 12 h before use. α,α -Bipyridyl (bpy, Shanghai Runjie Chemical Regent Co. Ltd, China, A.R.) was used as received. Poly(ethylene glycol) (PEG, $M_{n,th}$ = 1000, 2000, 4000, 6000; $M_{n,GPC}$ = 1400, 2840, 4030, 6010) was dried at 30 °C in vacuum for 24 h before use. Toluene, hexane, methanol, tetrahydrofuran (THF) and thionyl chloride (SOCl₂) were distilled before use.

2.2. Synthesis of macroinitiator Cl-PEG-Cl

Four kinds of macromolecular initiators (Cl-PEG-Cl) with different molecular weights ($M_{n,th}$ = 1000, 2000, 4000, 6000), with identification codes I–IV (Table 1), were prepared, respectively, through the reaction of PEG (20 mmol) with SOCl₂ (50 mmol) in toluene at the refluxing temperature for 24 h under dry nitrogen atmosphere. The yield was about 95%.

Table 1
GPC results of macromolecular initiators Cl-PEG-Cl

Macroinitiator ID	I	II	III	IV
M_n	1400	2830	4030	6010
M_w	1480	2990	4420	6430
M_w/M_n	1.06	1.06	1.10	1.07

2.3. Synthesis of block copolymer (PS-PEG-PS)

The block copolymerization was carried out in a baked three-necked round-bottomed flask equipped with a magnetic stirring bar according to a typical ATRP method [19,20]. The mixed solution of macroinitiator (MI), CuCl, bpy ligand and styrene monomer ($[MI]_0/[CuCl]_0/[bpy]_0/[St]_0 = 1:2:6:300$ (mol/mol)) was degassed for three times and then sealed and put into a oil bath preset at 130 °C to react for about 15 h.

2.4. Characterization of block copolymer PS-PEG-PS

The molecular weights of the copolymers were determined by gel permeation chromatography with a Waters Breaze GPC system (column: Ultrastaygel[®] 500 Å; calibration standards: linear homo-PS) in THF at 40 °C. Their ¹H NMR spectra were recorded in CDCl₃ at room temperature on a Varian Unity Inova 500 MHz spectrometer. Fourier transform infrared (FTIR) spectra were collected with a Nicolet 210 FTIR spectrometer (KBr). Differential scanning calorimetric (DSC) traces were recorded on a NETZSCH DSC 204 analyzer at a heating rate of 15 °C/min under nitrogen atmosphere. Indium (purity > 99.999%) was used to act the standard reference material for calibration.

2.5. Preparation of PS-PEG-PS based gas sensing composites

To improve the dispersion of carbon black (CB) in PS-PEG-PS, PEG2000 ($M_{n,th}$ = 2000) was pre-grafted onto the filler particles to produce CB-*g*-PEG2000 according to the route described in Refs. [4,21]. The typical grafting procedures are described as follows.

Firstly, introduction of carboxyl groups onto CB surface was achieved by treatment with ACPA in THF solution under nitrogen at 70 °C for 48 h. Then, the PEG was grafted onto the CB surface by direct condensation of carboxyl groups on the CB surface with terminal hydroxyl groups of PEG using DCC as a condensing agent in THF solution under nitrogen at 60 °C for 48 h. The grafting percentage is about 15% by weight.

When preparing PS-PEG-PS based composites, certain amount of CB-*g*-PEG2000 was dispersed in THF and treated by ultrasonic agitation for 30 min. Afterwards, the solution of PS-PEG-PS copolymer in THF was added into the CB suspension with a fast stirring for 30 min at 50 °C and then ultrasonic dispersion for additional 30 min. Eventually, the paste compound was coated onto a glass electrode. The measurements of resistance variation of the composites in response to organic solvent vapors were described in detail in our previous work [17]. The corresponding responsivity is characterized by the ratio of the transient resistance to the initial resistance in air.

Wide-angle X-ray diffraction (WAXD) patterns were recorded with a RIGAKU D/MAX 2200 diffraction instruments. To examine the real-time variation in supramolecular structure of the matrix polymer, the specimens were sealed in a polyethylene (PE) bag full of the testing solvent vapor during the WAXD measurement.

Table 2
GPC results of triblock copolymers PS-PEG-PS

Copolymer	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n	Macro-initiator	$x/(x+y)^a$ (%)
PS-PEG-PS (I)	2.11	3.23	1.53	I	14.4
PS-PEG-PS (II)	2.03	3.19	1.57	II	27.7
PS-PEG-PS (III)	2.31	4.17	1.80	III	33.3
PS-PEG-PS (IV)	2.41	3.80	1.58	IV	44.0

^a $x/(x+y)$ means the percent content of PEG segments ($-\text{CH}_2\text{CH}_2\text{O}-$) in the copolymer chains calculated from the GPC data. x is the amount of PEG ($-\text{CH}_2\text{CH}_2\text{O}-$), and y the amount of PS ($-\text{CH}_2\text{C}(\text{ph})\text{H}-$).

3. Results and discussion

3.1. Synthesis and characterization of PS-PEG-PS copolymer

The GPC results of the PS-PEG-PS copolymers initiated by different macroinitiators (I–IV) are listed in Table 2. Evidently, the molecular weights of the copolymers are similar and molecular weight distributions are relatively

consistent, which helps to get rid of the influence of molecular weight and polydispersity in the subsequent gas sensibility tests. Meanwhile, it is seen that the four copolymers have different contents of crystalline PEG segments, as indicated by a simple estimation from the GPC results.

The GPC curves of the copolymers initiated by different macroinitiators (I–IV) are shown in Fig. 1, respectively. Most of the GPC traces are symmetric and only a few have a shoulder toward low molecular weight. This indicates that the polymerizations of styrene initiated with the macroinitiators have given the desired copolymers and the unreacted macroinitiators or diblock copolymers are exiguous. It is worth noting that the molecular weight distributions of the copolymers are not narrow enough. It should result from the lower initiation efficiency of $-\text{Cl}$ groups of the macroinitiators, or incomplete conversion of the $-\text{OH}$ groups into $-\text{Cl}$ in the macroinitiators, or thermally initiated radical polymerization of styrene, or chain termination by coupling. Besides, the case of only one end group of $\text{Cl}-\text{PEG}-\text{Cl}$ initiated might also be involved.

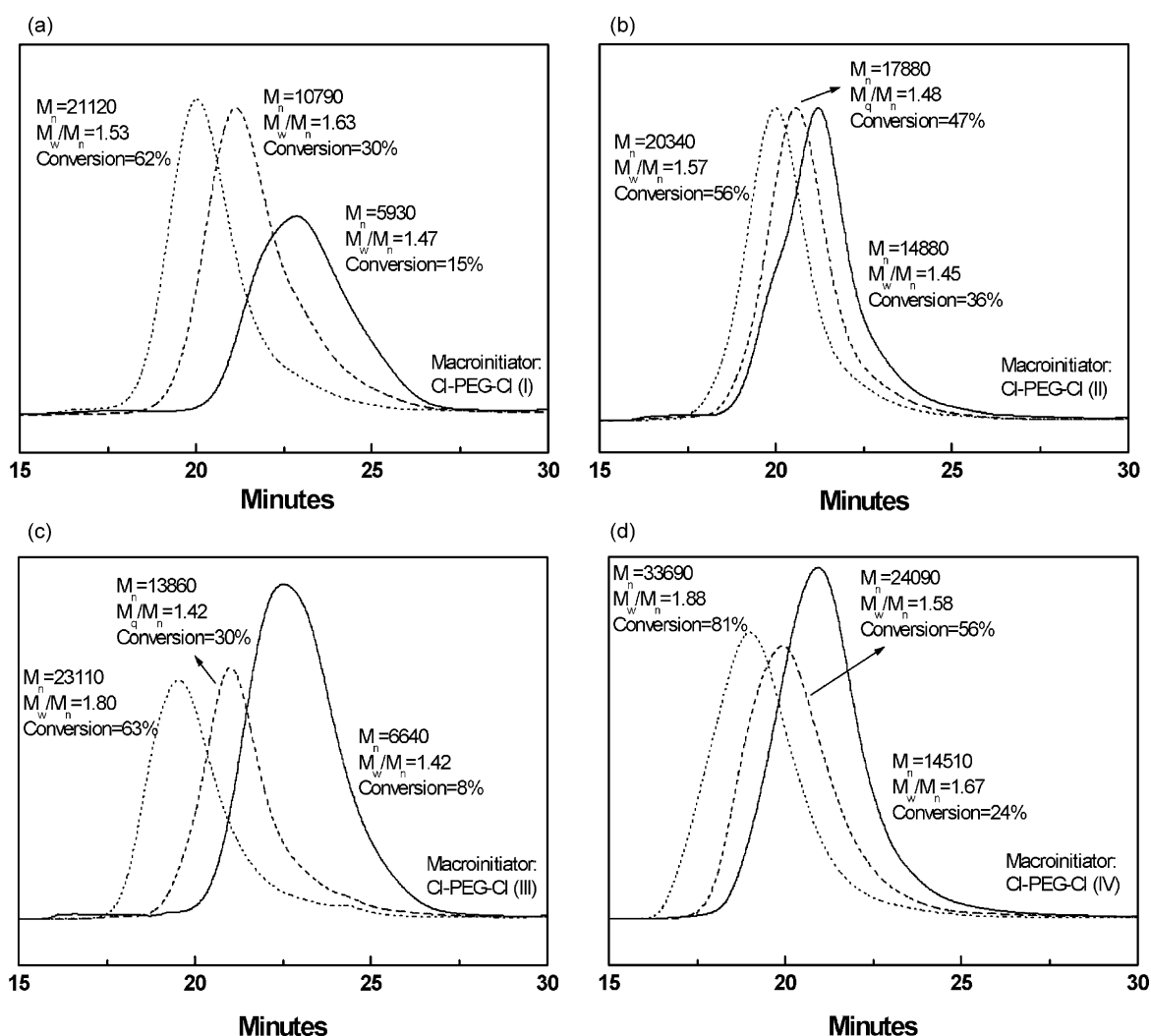


Fig. 1. GPC curves of typical copolymers obtained in the bulk polymerization of styrene at different conversions initiated by different macroinitiators (I–IV) in the presence of CuCl and bpy at $130\text{ }^\circ\text{C}$.

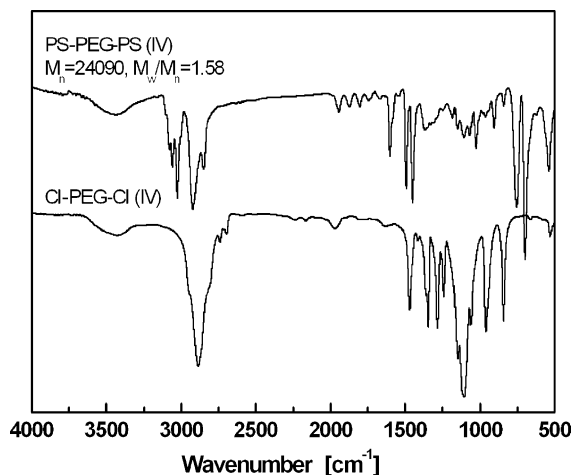


Fig. 2. FTIR spectra of macroinitiator (IV) and block copolymer PS-PEG-PS (IV) obtained in the polymerization of styrene initiated by macroinitiator (IV).

Fig. 2 illustrates the FTIR spectra of macroinitiator IV and the corresponding copolymer PS-PEG-PS (IV). It is found that not only the characteristic absorption peaks of PEG at 1151 and 965 cm^{-1} , but also the scattering of benzene ring at 1600, 1449 and 1491 cm^{-1} appear on the FTIR curve of the copolymer. The observation strongly suggests that the resultant polymer is the copolymer of PEG and styrene.

Typical ^1H NMR spectrum of copolymers PS-PEG-PS given in Fig. 3 again indicates that the product of interests is the copolymer of PEG and styrene. Besides, the PEG contents in the copolymer can also be estimated from the ^1H NMR spectral data. They are 1.5, 2.8, 4.3 and 6.7% for PS-PEG-PS (I–IV), respectively. Clearly, the copolymers have more and more PEG segments with a rise in the molecular weight of the macroinitiator, as revealed by the GPC experiments. It is noteworthy that although the PEG compositions given by GPC and ^1H NMR show

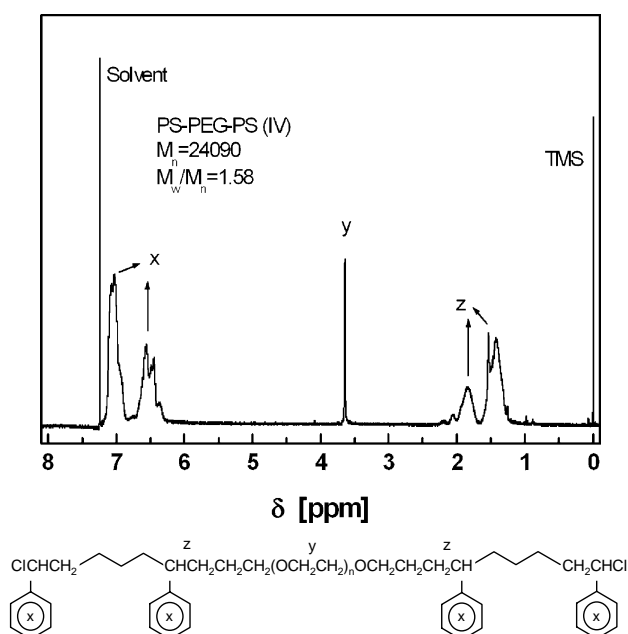


Fig. 3. ^1H NMR spectra of block copolymers PS-PEG-PS (IV) obtained during the polymerization of styrene initiated by the macroinitiator (IV).

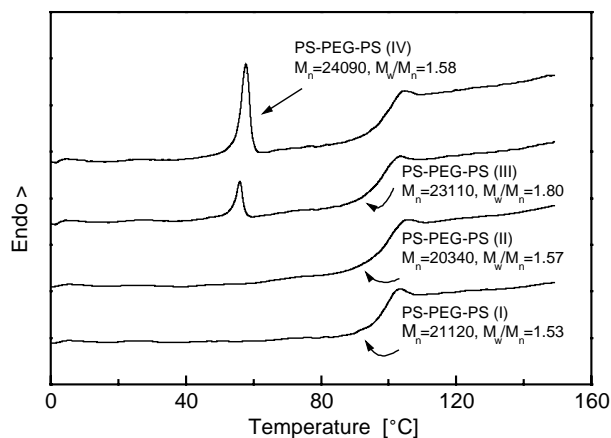


Fig. 4. DSC heating traces of block copolymers PS-PEG-PS (I–IV) with similar molecular weights initiated by different macroinitiators (I–IV) in the presence of CuCl and bpy at 130 $^{\circ}\text{C}$.

similar dependence on the molecular weight of the macroinitiator, the two groups of data are not the same. Because of the influence of the absorbed H_2O and the PEG chains, the results calculated from ^1H NMR are not very accurate. Furthermore, it might be due to the impure resultant of the copolymerization, which contains homopolymerized PS and diblock or multiblock copolymers as deduced from the higher polydispersities of the products. These factors might lead to lower PEG contents calculated by the ^1H NMR data than those by GPC. Similar phenomena can be found in Feng and Pan's work [22].

Considering that PEG is a crystalline polymer, it is worth measuring the melting behavior of the copolymers to check whether they have acquired crystallizability as planned. From the DSC heating traces in Fig. 4, it is seen that the melting peaks of the crystalline phase of PEG appear only for copolymers III and IV, which hold the longest PEG segments, and the glass transition of PS is perceivable for all investigated samples. When the amount of PEG segments in the copolymer is fixed, the endothermic peak height increases with decreasing the molecular weight of the copolymer, i.e. with decreasing the length of PS segments (Fig. 5). All these results show that

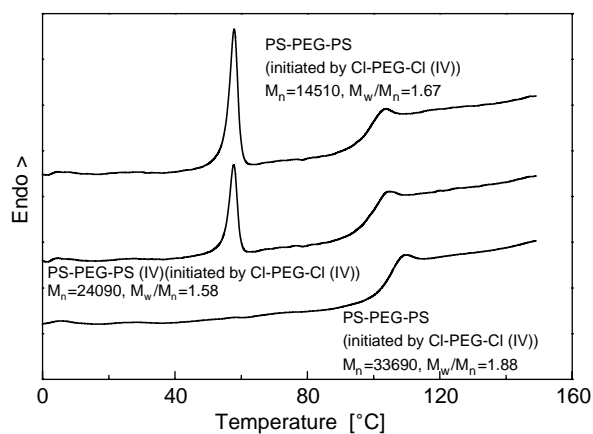


Fig. 5. DSC heating traces of block copolymers PS-PEG-PS with different molecular weights initiated by macroinitiator (IV) in the presence of CuCl and bpy at 130 $^{\circ}\text{C}$.

the synthesized copolymers fit the requirements of the present study. By estimating the areas of the melting peaks of copolymers III and IV on the DSC curves by an integration procedure, it is known that the enthalpies of melting are 0.6093 and 2.016 J/g, respectively. Assuming that there is a simply linear correlation between the amount of normalized crystalline phase and the amount of PEG in the copolymers, the DSC integration areas of the crystalline phase in copolymers I and II would be less than zero on the basis of a rough extrapolation. Clearly, it is unauthentic. An acceptable explanation might be that under the investigated experimental conditions the ability of PEG in copolymers to crystallize is no longer available when its chain length is shorter than a critical value. The mass of amorphous PS in the copolymers hinders crystallization of PEG chains.

The glass transition temperatures of PS in the copolymers are nearly not dependent on the ratios between PS and PEG chains. As exhibited by the DSC analysis in Fig. 4, the T_g values of PS in the copolymers I–IV are 97.4, 98.3, 96.6 and 98.4 °C, respectively, which are close to the T_g of pure PS (90–100 °C, depending on molecular weight). This means that the PEG chains do not have significant effect on the segments movement of PS. It can be attributed to the lower molecular weight of PEG as compared to that of PS in the copolymers.

3.2. Conductive property of PS–PEG–PS based composites

On the basis of above study, it is known that the triblock copolymers PS–PEG–PS with desired compositions have been synthesized. Therefore, four copolymers PS–PEG–PS (I–IV) with similar molecular weights ($M_n \sim 2 \times 10^4$) but different PEG fractions (14–44%) were used as the matrices (Table 2) for producing conductive composites filled with CB-g-PEG2000. It is believed that the role of the crystalline phases in the conducting composite materials can thus, be highlighted.

Fig. 6 illustrates the electrical resistivity of the CB-g-PEG2000/PS–PEG–PS composites as a function of CB loading. The resistivity of the composites decreases with increasing CB content, showing a typical percolation effect.

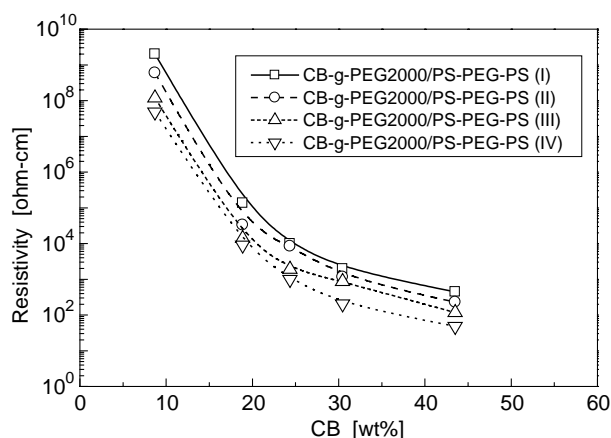


Fig. 6. Electrical resistivity of CB-g-PEG2000/PS–PEG–PS composites as a function of CB content.

Besides, the resistivity of the composites also decreases with a rise of PEG content in the matrices at equal CB concentrations. In other words, higher CB content is needed to reach equal conductivity for the composites with PS–PEG–PS having lower PEG fraction. This proves that the microstructures of these composites are very similar. The conductive additives were pushed to the crystalline domain boundaries and the increase of the crystalline phase content led to increased effective contacts among the fillers, and hence reduced percolation thresholds.

When the composites are exposed to organic solvent vapors, rapid increase in the resistance can be found, demonstrating the gas sensitivity of the materials (Fig. 7). The composites resistance can be further recovered in case the samples are removed to air, which allows desorption of the absorbed solvent vapors. The reversible variation in electrical resistance of the materials shows the potential of the composites serving as candidates for gas sensors. A careful survey of Fig. 7 reveals that the response patterns are different in different vapors, which factually reflects the possibility of solvent discrimination. Further investigation on this topic will be conducted in another paper of the authors.

3.3. Effect of crystalline phases on gas sensitivity of PS–PEG–PS based composites

To have a comprehensive image of the composites' responsivity against solvent vapors, Fig. 8 shows the maximum responsivity of the composites as a function of CB concentration and matrix species. In most cases there is a peak value at the CB content dependence of the maximum responsivity. This is because lower CB concentration would enhance the probability of partial discontinuance of the contacted CB driven by the swollen matrix while less amount of the matrix facilitates solvent diffusion and hence matrix swelling. The competition between the two opposite factors leads to the appearance of the peak-like dependence of maximum responsivity on CB content [17].

It is interesting to note that in a given solvent vapor, the optimum content of CB, at which the composites have the highest maximum responsivity, decreases with increasing the PEG content in the matrix. That is, the optimum content of CB of CB-g-PEG2000/PS–PEG–PS (IV) system is the lowest. It is understandable as viewed from the percolation curves in Fig. 6, because the higher the fraction of the crystalline PEG phase, the lower CB loading is required to construct sufficient conducting paths.

In addition, Fig. 8 manifests that the maximum responsivity of the composites is quite different under the same experimental conditions in spite of the fact that the matrix polymers have almost the same molecular weights and compositions (Table 2). Naturally, the ratio of PEG/PS in the copolymers used as the matrix should take the responsibility. For the convenience of discussion, values of the maximum responsivity of the composites at the optimum contents of CB are plotted as a function of PEG content in the matrix polymer in Fig. 9. It is clear that an increased PEG content leads

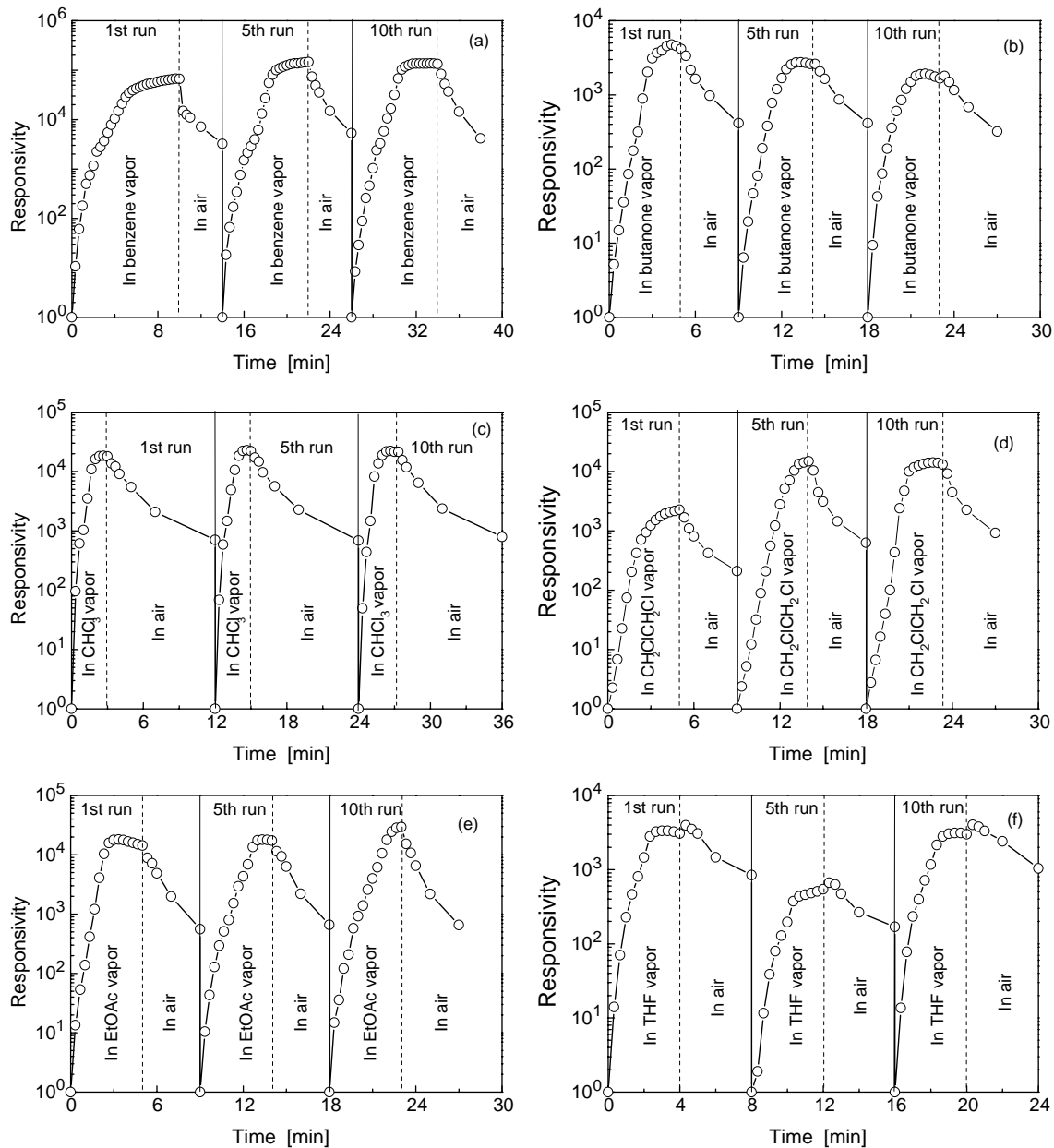


Fig. 7. Responsivity of CB-g-PEG2000/PS-PEG-PS (IV) composites against various solvent vapors (testing temperature: 40 °C, CB content: 19 wt%). The dash lines define the vapor absorption and desorption zones.

to higher maximum responsivity in most cases. Since the copolymers have similar molecular weights, a rise in the PEG content corresponds to decreased lengths of the PS segments. If swelling of the amorphous portions (rather than the crystalline ones) of the matrix polymer is responsible for the drastic variation in electrical resistance of the conducting composites, it can be reasonably deduced that the composites with shorter PS segments (i.e. longer PEG segments) are easier to swell up when other conditions are identical. This explains the reason why PS-PEG-PS (IV) based composites possess the highest maximum responsivity against the solvent vapors. To verify the aforesaid assumption dealing with swelling performance of crystalline phases in the copolymers, a series of WAXD tests were carried out as follows. The experiments

were made simply on the basis of the fact that when the polymer crystals are swollen or dissolved by organic solvent vapors, the intensities or shapes of their X-ray diffraction peaks should change accordingly.

For purposes of systematic research, the WAXD spectra of neat PEG, neat PS and PS-PEG-PS copolymer in air and solvent vapors are plotted in Figs. 10–12, respectively. By comparing the spectra of these polymers recorded in air, it is known the spectra of these polymers recorded in air, it is known the main diffraction at 19° is the characteristic peak of PEG, and that at 22° belongs to the PE bag for holding the samples. Besides, PS shows a wide scattering from 15 to 25°. The diffraction spectrum of PS-PEG-PS can be regarded as the sum of the spectra of PEG and PS as expected.

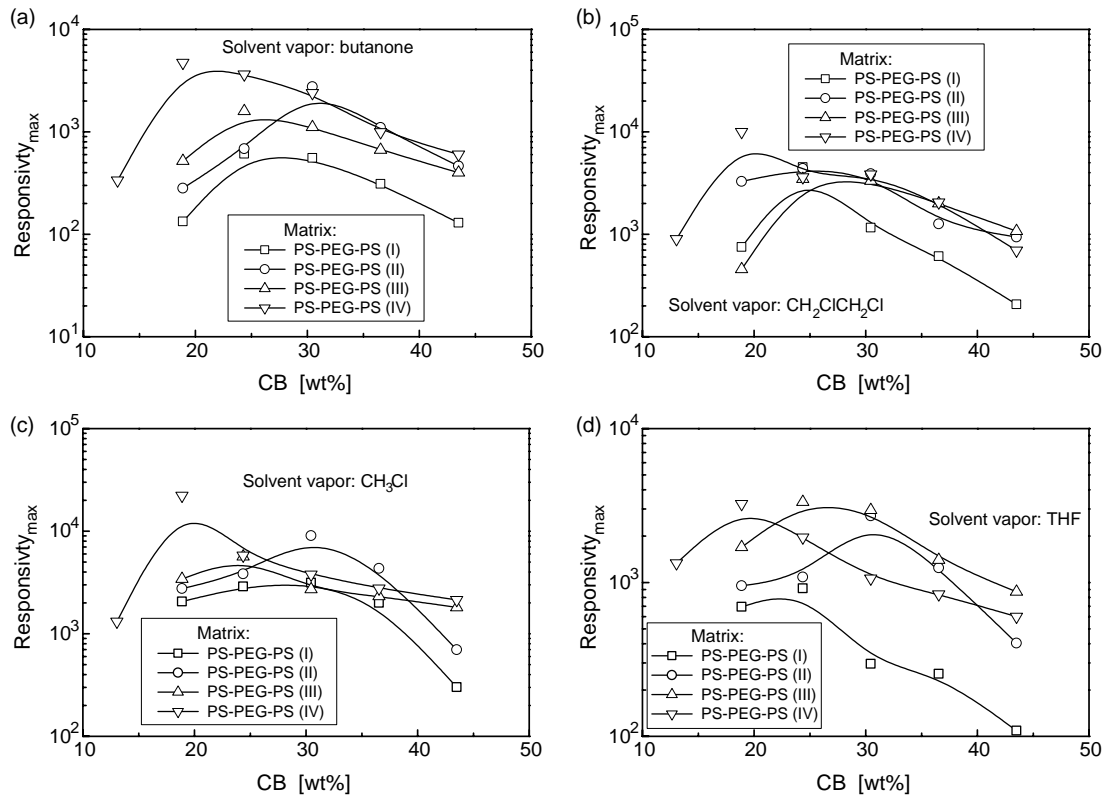


Fig. 8. Effect of CB content on the maximum responsivity of CB-g-PEG2000/PS-PEG-PS composites against various solvent vapors (testing temperature: 40 °C).

Fig. 12 collects the WAXD patterns of PS-PEG-PS (IV) before and after being exposed to the solvent vapor. In comparison to the curve of the original specimen (curve 1 in Fig. 12), no evident changes in either the diffraction intensities or the spectrum profiles can be observed (curves 2, 3, and 4 in Fig. 12). According to the data shown in Fig. 7(f), when PS-PEG-PS (IV) based composites were removed from air into THF vapor, the resistance increased by several orders of magnitude within 4 min. However, it seems to have nothing to do with the results of Fig. 12. Therefore, it is known that the crystalline PEG could not be swollen or dissolved by the organic vapor within the time of

interests. On the other hand, the WAXD spectra of the composites transferred from THF vapor to air (curves 5 and 6 in Fig. 12) also evidence this conclusion. With the lapse of time, the solvent absorbed by the specimen should be gradually desorbed in air. If the crystalline portions in the matrix polymer were somewhat swollen, recrystallization would take place when the composites meet air. Clearly, this is not the case. It implies that the contribution of the crystalline phase to resistance change of the composites in solvent vapors is negligible. Since considerable weight increase is associated with the resistance increase of the composites in solvent vapors [23], swelling or partial

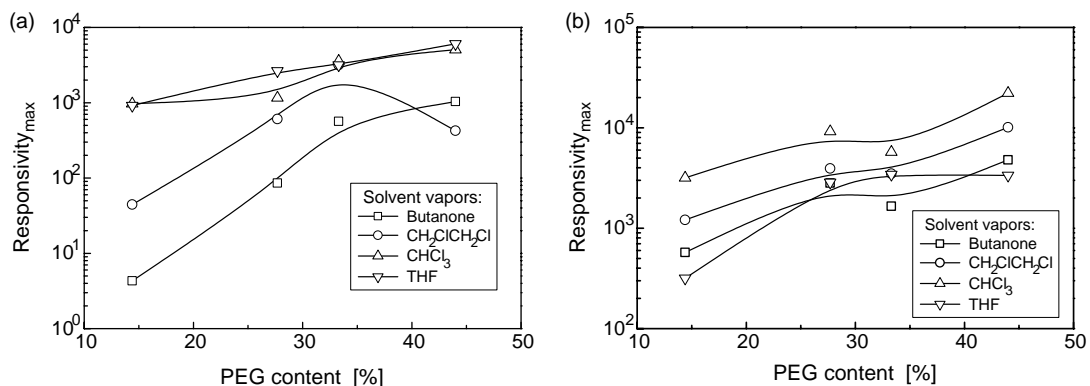


Fig. 9. Effect of PEG fraction in the matrix polymer on the maximum responsivity of CB-g-PEG2000/PS-PEG-PS composites at the optimum contents of CB against different solvent vapors. Testing temperature: (a) 30 °C, (b) 40 °C.

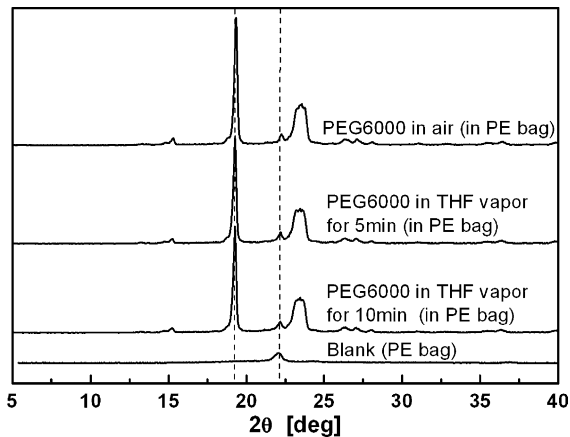


Fig. 10. X-ray diffraction spectra of PEG6000 ($M_{n,th}=6000$).

dissolve of the amorphous phases of the matrix polymer should be the controlling factor for the electrical response behavior.

4. Conclusions

A series of triblock copolymer PS-PEG-PS with pre-determined molecular weights and relatively narrow molecular weight distribution were successfully synthesized by ATRP method. Through tuning the segment ratio between crystalline PEG and amorphous PS, the crystallinity of the copolymer can be finely changed.

By using the above copolymers as matrices, CB filled composite materials were prepared, in which the matrix polymers have similar molecular weight and molecular weight distribution but different amounts of the crystalline portions (i.e. PEG segments). In addition to the high responsivity against solvent vapors as characterized by the rapid increase in the electrical resistance, the gas sensitivity of the composites is highly dependent on the fraction of the crystalline phases in the matrices. An increase in the crystalline phases content results in higher responsivity at lower CB concentration due to the increased effective filler concentration in the amorphous phases. The crystalline phases in the matrix polymer cannot

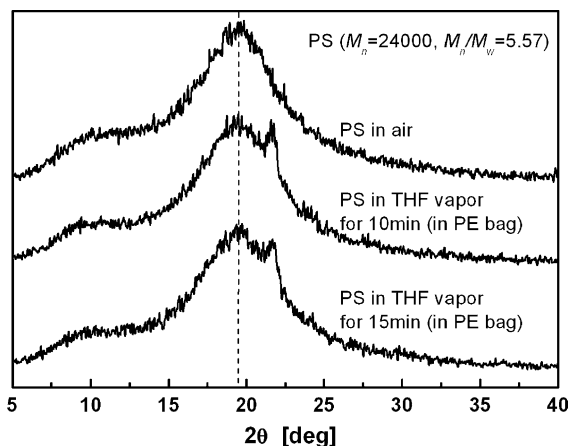


Fig. 11. X-ray diffraction spectra of PS.

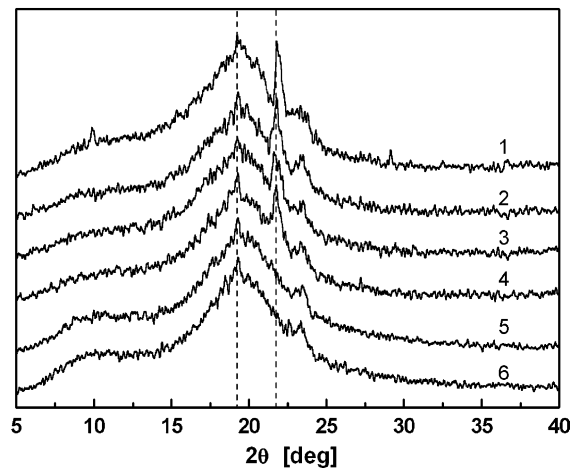


Fig. 12. X-ray diffraction spectra of PS-PEG-PS (IV). Samples: 1, PS-PEG-PS (IV) in air (in PE bag); 2, PS-PEG-PS (IV) in THF vapor for 15 min (in PE bag); 3, PS-PEG-PS (IV) in THF vapor for 20 min (in PE bag); 4, PS-PEG-PS (IV) in THF vapor for 25 min (in PE bag); 5, PS-PEG-PS (IV) that had been saturated with THF vapor and then transferred to air for 3 min; 6, PS-PEG-PS (IV) that had been saturated with THF vapor and then transferred to air for 13 min.

be swollen when the composites exhibit drastic resistance variation. Solvent vapor induced volume expansion of the amorphous phases in the matrix polymer should account for the breakdown of the conductive networks formed by the contacted CB particles, and hence the gas sensitivity.

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References

- [1] Zhang MQ, Zeng HM. In: Olabisi O, editor. Conducting thermoplastics composites. Handbook of thermoplastics. New York: Marcel Dekker; 1997. p. 873–91.
- [2] Chen J, Tsubokawa N. Electric properties of conducting composite from poly(ethylene oxide) and poly(ethylene oxide)-grafted carbon black in solvent vapor. *Polym J* 2000;32:729–36.
- [3] Chen J, Tsubokawa N. A novel gas sensor from polymer grafted carbon black: responsiveness of electric resistance of conducting composite from LDPE and PE-*b*-PEO-grafted carbon black in various vapors. *Polym Adv Technol* 2000;11:101–7.
- [4] Chen J, Tsubokawa N. Novel gas sensor from polymer grafted carbon black: vapor response of electric resistance of conducting composites prepared from poly(ethylene-*block*-ethylene oxide)-grafted carbon black. *J Appl Polym Sci* 2000;77:2437–47.
- [5] Chen J, Tsubokawa N, Maekawa Y, Yoshida M. Vapor response properties of conducting composites prepared from crystalline oligomer-grafted carbon black. *Carbon* 2002;40:1602–5.
- [6] Feller JF, Langevin D, Marais S. Influence of processing conditions on sensitivity of conductive polymer composites to organic solvent vapours. *Synth Met* 2004;144:81–8.

- [7] Srivastava S, Tchoudakov R, Narkis M. A preliminary investigation of conductive immiscible polymer blends as sensor materials. *Polym Eng Sci* 2000;40:1522–8.
- [8] Doleman BJ, Lonergan MC, Severin EJ, Vaid TP, Lewis NS. Quantitative study of the resolving power of arrays of carbon black-polymer composites in various vapor-sensing tasks. *Anal Chem* 1998;70:4177–90.
- [9] Albert KJ, Lewis NS, Schauer CL, Sotzing GA, Stitzel SE, Vaid TP, et al. Cross-reactive chemical sensor arrays. *Chem Rev* 2000;100:2595–626.
- [10] Chen SG, Hu JW, Zhang MQ, Li MW, Rong MZ. Gas sensitivity of carbon black/waterborne polyurethane composites. *Carbon* 2004;42:645–51.
- [11] Zee F, Judy JW. Micromachined polymer-based chemical gas sensor array. *Sens Actuators, B Chem* 2001;72:120–8.
- [12] Partridge AC, Jansen ML, Arnold WM. Conducting polymer-based sensors. *Mater Sci Eng, C: Bio Sci* 2000;12:37–42.
- [13] Doleman BJ, Severin EJ, Lewis NS. Trends in odor intensity for humans and electronic noses: relative roles of odorant vapor pressure vs. molecularly specific odorant binding. *Proc Natl Acad Sci USA* 1998;95:5442–7.
- [14] Dong XM, Fu RW, Zhang MQ, Zhang B, Li JR, Rong MZ. A novel sensor for organic solvent vapors based on conductive amorphous polymer composites: carbon black/poly(butyl methacrylate). *Polym Bull* 2003;50:99–106.
- [15] Dong XM, Fu RW, Zhang MQ, Zhang B, Rong MZ. Carbon black filled poly(2-ethylhexyl methacrylate) as a candidate for gas sensing material. *J Mater Sci Lett* 2003;22:1057–9.
- [16] Dong XM, Fu RW, Zhang MQ, Zhang B, Li JR, Rong MZ. Vapor induced variation in electrical performance of carbon black/poly(methyl methacrylate) composites prepared by polymerization filling. *Carbon* 2003;2:371–4.
- [17] Li JR, Xu JR, Zhang MQ, Rong MZ. Carbon black/polystyrene composites as candidates for gas sensing materials. *Carbon* 2003;41:2353–60.
- [18] Tsarevsky NV, Sarbu T, Gölbelt B, Matyjaszewski K. Synthesis of styrene-acrylonitrile copolymers and related block copolymers by atom transfer radical polymerization. *Macromolecules* 2002;35:6142–8.
- [19] Wang J, Matyjaszewski K. Controlled/‘living’ radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes. *J Am Chem Soc* 1995;117:5614–5.
- [20] Wang J, Matyjaszewski K. Controlled/‘living’ radical polymerization. Halogen atom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process. *Macromolecules* 1995;28:7901–10.
- [21] Okazaki M, Maruyama K, Tsuchida M, Tsubokawa N. A novel gas sensor from poly(ethylene glycol)-*graft* carbon black: responsibility of electric resistance of poly(ethylene glycol)-*graft* carbon black against humidity and solvent vapor. *Polym J* 1999;31:672–6.
- [22] Feng X, Pan C. Block and star copolymers by mechanism transformation. 7. Synthesis of polytetrahydrofuran/poly(1,3-dioxepane)/polystyrene ABC miktoarm star copolymers by combination of CROP and ATRP. *Macromolecules* 2002;35:2084–9.
- [23] Li JR. Gas sensitivity of carbon black/polystyrene series conductive composites. PhD Thesis, Zhongshan University; 2004.