Poly(styrene-*co*-vinylbenzophenone) as Photoactive Antimicrobial and Selfdecontaminating Materials

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ABSTRACT: Photoactive structures such as benzophenone chromophoric groups were incorporated onto polymers by using a Friedel-Crafts acylation reaction. The structures and properties of the resultant polymers, poly (styrene-*co*-vinylbenzophenone) were evaluated as the ratio of benzoyl chloride to phenyl groups in polystyrene in the acylation bath increased. The results proved that the poly (styrene-*co*-vinylbenzophenone) in different contents of benzophenone groups was successfully prepared, and the contents of the benzophenone chromophoric group branched in the resultant polymer increased as the amount of benzoyl chloride in acylation bath increased. Also, the poly (styrene-*co*-vinylbenzophenone) copolymers revealed superior special activities such as antibacterial ability. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3173–3179, 2008

Key words: poly(styrene-*co*-vinylbenzophenone); selfdecontamination; Friedel-Crafts acylation; radical; polystyrene; benzophenone

INTRODUCTION

As an effort of prevention of cross-transmission of infectious disease through surface contact, different refreshable biocidal polymeric materials have been synthesized.[1–4] More recently, benzophenone containing cellulose were demonstrated excellent abilities to provide durable antibacterial properties under weak UV (UVA; 365-nm wavelength light) irradiation, which are particularly promising to be employed on medical textiles.[5,6] The antibacterial functions from the benzophenone structures are due to radicals produced under the light irradiation. Generally, radicals have short life and tend to undergo fast reactions, since they are highly reactive chemical species possessing at least one unpaired electron.[7] Many chemical and biological processes involve radical reactions, such as the biological reduction of O_2 by antioxidants and radical polymerization of unsaturated molecules to polymers. In particular, benzophenone chromophoric groups, known to undergo n → π* transition by photo-exposure, are commonly used as photosensitizers in photochemistry. Intersystem crossing from the initial singlet to triplet state is known to occur efficiently in the ketone site of benzophenone and derivatives, and the activated ketone site is highly reactive toward abstracting hydrogen atom from weak C—H bond or other hydrogen donor to form a ketyl radical and can be readily quenched by oxygen.[8,9] Because of high reactivity of the formed radicals, the photo-excited benzophenone polymers demonstrated the selfdecontaminating functions under longer wavelength UV exposure against certain toxic chemicals and kill microorganisms.[5,6]

According to the above results, polymers containing benzophenone chromophoric groups could be biocidal coating materials when exposed to longer wavelength UV as well. Based on such expectation, this study was to develop effective biocidal materials with improved performance. Thus, polymers containing the specific groups were synthesized and characterized by various instrumentations to prove the structure and properties. The synthesis path is depicted in Scheme 1, and the resultant polymers were characterized as poly (styrene-*co*-vinylbenzophenone).
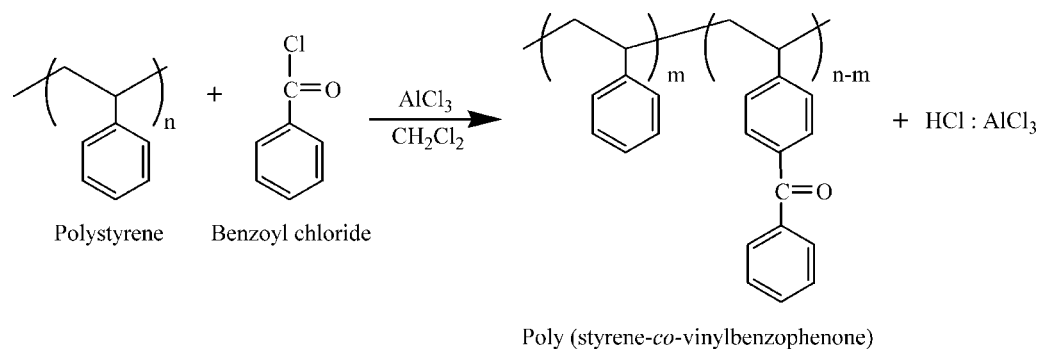
EXPERIMENTAL

Materials

Polystyrene (typical M_n 140,000; typical M_w 230,000) was purchased from Aldrich (MO). Benzoyl chloride (ACS reagent), Aluminum chloride (AlCl$_3$) (anhydrous, powder 98.5%), and potassium sodium tartrate (p.a.) were purchased from Acros (NJ). Dichloromethane (Biosynthesis grade, EM science,

Scheme 1 Friedel-Crafts acylation reaction of polystyrene and benzoyl chloride.

NJ) was used as a system solvent and all the reagents were used as received without further purification.

Preparation

The acylation was carried out in a round bottom flask equipped with a condenser and a magnetic stirrer at room temperature. The system was purged with nitrogen gas to expel air and moisture, and the nitrogen atmosphere was remained during the acylation process. Then, a dichloromethane solution containing benzoyl chloride was added into another dichloromethane solution containing AlCl$_3$. The mixture was stirred for 2 h, afterward, a 100 mL of dichloromethane solution containing various concentrations of polystyrene solution was drop wise added to the benzoyl chloride and AlCl$_3$ mixture under stirring. The concentrations of polystyrene were set to be the ratio of benzoyl chloride to phenyl groups in polystyrene into 0.5 : 1, 1 : 1, 2 : 1, and 4 : 1 in the acylation bath, respectively. After stirring for 24 h, the reaction mixture was poured on to a bath containing potassium sodium tartrate aqueous solution, and the mixture was stirred for 3 h again. Then, the mixture solution was filtered to separate AlCl$_3$ from the mixture. The resultant polymer, poly (styrene-*co*-vinylbenzophenone) copolymer in dichloromethane was collected by a separation funnel. The poly (styrene-*co*-vinylbenzophenone) was directly cast into films by evaporating dichloromethane. On the other hand, a ultra-violet (UV) lamp (BLE-8 T365, Ultraviolet spectonics, NY, USA) or the just daylight was used for the photoactivation treatment.

Characterization

Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Electron, USA) with a resolution of 4 cm^{-1}, and measurements were carried out by using KBr pellets. UV–vis absorption spectra were taken with an Evolution 600 UV–visible spectrophotometer (Thermo Scientific, USA) in a wavelength range of 200–800 nm with a 1-cm quartz cell. Nuclear magnetic resonance (NMR) was conducted with a Bruker Advance 500 MHz NMR spectrometer using CDCl$_3$ as a solvent. The thermal behavior of polymers were characterized using differential scanning calorimetry (DSC), performed on a Shimadzu DSC-60 (Shimadzu, USA) under nitrogen atmosphere with programmed heating of 10°C/min. X-ray diffraction (XRD) measurements were performed at room temperature with Cu Kα X-rays (α = 1.5418 Å) with a D8 Advance (Bruker, Germany). θ-theta wide angle goniometer was used and the ultimate peak resolution was 2θ = 0.025°. Data were recorded from 10 to 30° in steps of 0.02°. Electron paramagnetic resonance (EPR) spectra of the polymer samples were recorded under room temperature conditions operating at X-band (9 GHz) frequency on a Bruker ECS 106 spectrometer. The antimicrobial properties of poly (styrene-*co*-vinylbenzophenone) (powder state) were tested against *Staphylococcus aureus* (*S. aureus*) (ATCC 12600, a gram-positive bacterium) and *Escherichia coli* (*E. coli*) (K-12, a gram-negative bacterium) according to a shaking flask method (DOW0923). During the contact time, the diluted microbial aqueous solution contained the resultant polymer was illuminated under UV light (wavelength: (365 nm; intensity: 1850 μW/cm^2) for 1 h, which could initiate radicals in the poly (styrene-*co*-vinylbenzophenone). The same testing procedure was employed for polystyrene, serving as a control. After the contact time, the microbial aqueous solution was injected in agar plate and it was incubated at 37°C for 18 h. The reduction of bacteria was calculated according to the following eq. (1).

$$\text{Reduction of bacteria (\%)} = \frac{(B - A)}{B} \times 100 \quad (1)$$

where, A and B are the surviving cells (colony forming unit mL^{-1}) for the plates containing test sample (poly (styrene-*co*-vinylbenzophenone)) and the control (polystyrene), respectively.
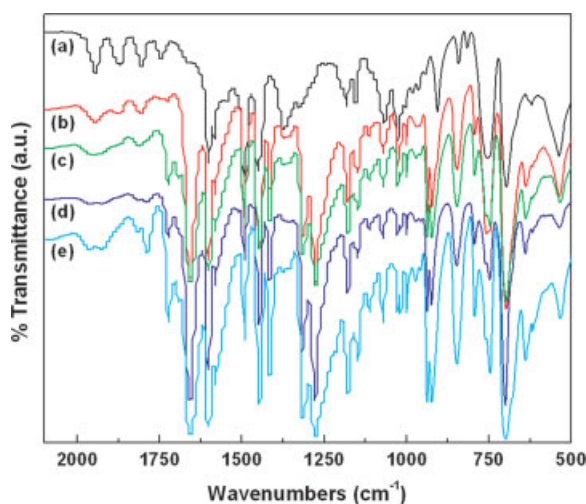
Figure 1 FTIR spectra of pristine polystyrene (a) and poly (styrene-*co*-vinylbenzophenone) with various ratios of benzoyl chloride to phenyl groups in polystyrene as 0.5 : 1 (b), 1 : 1 (c), 2 : 1 (d), and 4 : 1 (e). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 2 UV–vis spectra of pristine polystyrene (a) and poly (styrene-*co*-vinylbenzophenone) with various ratios of benzoyl chloride to phenyl groups in polystyrene as 0.5 : 1 (b), 1 : 1 (c), 2 : 1 (d), and 4 : 1 (e). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

RESULTS AND DISCUSSION

Structural properties of poly(styrene-*co*-vinylbenzophenone) copolymers

Figure 1 shows the FTIR spectra of pristine polystyrene [Fig. 1(a)] and poly (styrene-*co*-vinylbenzophenone) copolymers with various ratios of benzoyl chloride to phenyl groups in polystyrene, such as 0.5 : 1 [Fig. 1(b)], 1 : 1[Fig. 1(c)], 2 : 1[Fig. 1(d)], and 4 : 1[Fig. 1(e)], respectively. All spectra show the aromatic C=C stretch at around 1600 cm^{-1}. However, the spectra of poly (styrene-*co*-vinylbenzophenone) only show a carbonyl peak at 1655 cm^{-1}, and ketone bands at 1317 and 1275 cm^{-1}. On the other hand, geometric (cis/trans) isomerism is responsible for the ketone band split into two peaks and this phenomenon is also observed in aryl-C bending peak slitting into 935 and 920 cm^{-1} in the poly (styrene-*co*-vinylbenzophenone).[10–12] Also, as the content of benzoyl chloride increased in the acylation bath, the peak intensity of the poly (styrene-*co*-vinylbenzophenone) at 700 and 754 cm^{-1}, attributed to the out-of-plane C—H vibration of mono-substituted benzene ring, decreased, while the peak intensity at 850 cm^{-1} attributed to the out-of-plane C—H vibration of *para*-substituted benzene ring increased.[13] Therefore, it was assumed that poly (styrene-*co*-vinylbenzophenone) were successfully prepared and the benzophenone chromophoric groups created in the resultant polymers were increased as the content of benzoyl chloride increased in the acylation reaction.

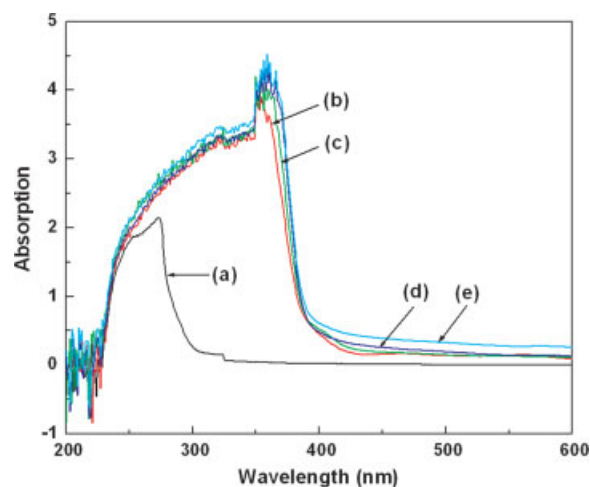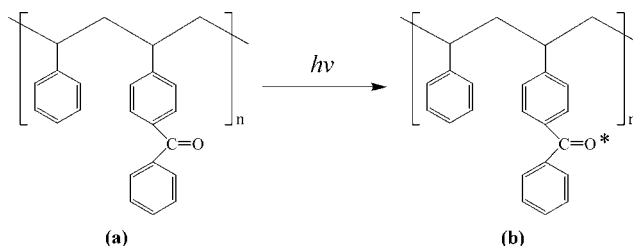Figure 2 shows the UV–vis spectra of pristine polystyrene and poly (styrene-*co*-vinylbenzophenone) with various ratios of benzoyl chloride to phenyl groups in polystyrene. It was observed that the poly (styrene-*co*-vinylbenzophenone) showed the long absorption tail of polyketone extending beyond 350 nm, allowing the light of this wavelength to induce n → π* transitions. Scheme 2 represents the proposed excitation process of the poly (styrene-*co*-vinylbenzophenone) carbonyl groups by 350 nm photons, where the structure on the left side [Scheme 2(a)] corresponds to poly (styrene-*co*-vinylbenzophenone) and the structure on the right side [Scheme 2(b)] is a representation of the triplet excited state.[8]

On the other hand, the radical activity of the poly (styrene-*co*-vinylbenzophenone) was observed by using an EPR spectrometer. EPR spectroscopy is a technique for studying chemical species that have one or more unpaired electrons. And it is the only direct way to detect and measure free radicals. As shown in Figure 3, poly (styrene-*co*-vinylbenzophenone) [Fig. 3(b)] exhibits a signal with a peak to peak line width (ΔHpp) of 14.8 G and a *g*-value of 2.0064 after UV light irradiation. This indicates that

Scheme 2 Excitation process of poly (styrene-*co*-vinylbenzophenone) under UV light.
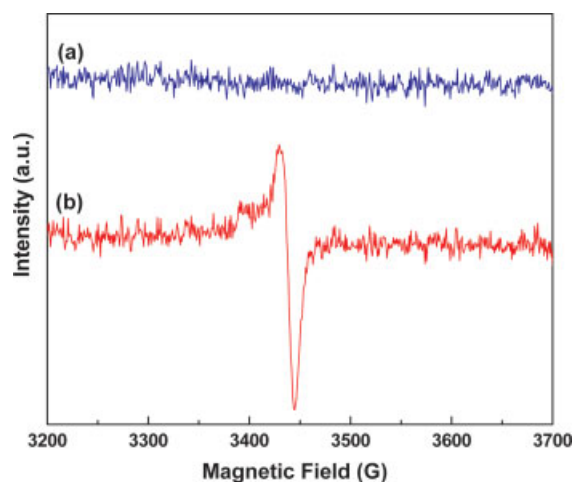
Figure 3 Evolution of the room-temperature EPR spectra of pristine polystyrene (a) and poly (styrene-*co*-vinylbenzophenone) (the ratio of benzoyl chloride to phenyl groups in polystyrene = 1 : 1) after UV irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

unpaired electrons or free radicals existed in the resultant polymer, which confirmed that the radicals were activated in the copolymer by the UV irradiation.

Grafting rate of benzophenone groups in poly(styrene-benzophenone) copolymers

^{1}H NMR analyses of pristine polystyrene and poly (styrene-*co*-vinylbenzophenone) containing different amount of benzophenone structures were performed to investigate the grafting yields of benzophenone chromophoric groups in the poly (styrene-*co*-vinylbenzophenone). Figure 4 shows ^{1}H NMR spectra of pristine polystyrene [Fig. 4(a)] and the copolymers; the ratios of benzoyl chloride to phenyl groups in polystyrene in reaction were 0.5 : 1 [Fig. 4(b)] and 4 : 1 [Fig. 4(c)]. The resonances at δ = 6.33–7.31 ppm are due to the aromatic protons of polystyrene chains,[14] and were observed in every spectrum of the copolymers as well as in the spectrum of pristine polystyrene. However, in the spectra of the copolymers, new peaks were created at around δ = 7.3–8.1 ppm, originated from benzophenone chromophoric groups in the poly (styrene-*co*-vinylbenzophenone).[15] On the other hand, some close correlation between the relative peak integral values and the content of benzoyl chloride in the acylation bath were observed in the NMR spectra. Therefore, the grafting rate of benzophenone chromophoric groups in the poly (styrene-benzophenone) copolymers were indirectly assumed from the peak integral ratio of the value at δ = 7.4–7.7 ppm (▲) to the value at δ = 7.0 ppm (●). And the data were statically treated by Boltsmann fit, as shown in Figure 5. It was observed that the relative

peak integral values, the ratios of the value at δ = 7.4–7.7 ppm to the value at δ = 7.0 ppm in the NMR spectra of the copolymers, increased with increasing the content of benzoyl chloride in the acylation bath. Therefore, it is an indication that the grafting rate of benzophenone chromophoric group in the resultant poly (styrene-*co*-vinylbenzophenone) increased as the content of benzoyl chloride in the acylation bath increased.

Thermal properties of copolymers

Thermal properties of pristine polystyrene and poly (styrene-*co*-vinylbenzophenone) with different amount of benzophenone structures were analyzed and compared as shown in Figure 6. The endothermal peaks
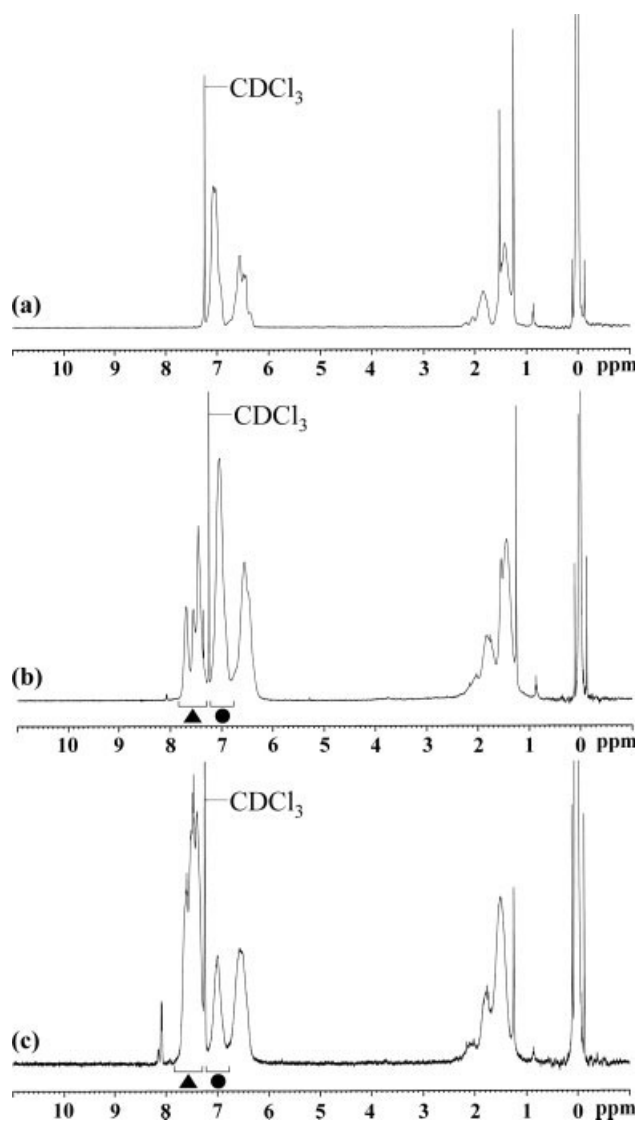

Figure 4 ^{1}H NMR spectra of pristine polystyrene (a) and poly (styrene-*co*-vinylbenzophenone); ratios of benzoyl chloride to phenyl groups in polystyrene = 0.5 : 1 (b) and 4 : 1 (c).
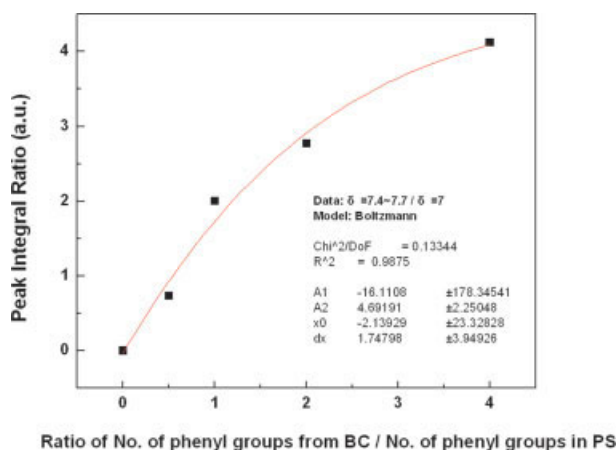
Figure 5 Peak integral ratios of the value at δ = 7.4–7.7 ppm to the value at δ = 7.0 ppm in ^{1}H NMR spectra of poly (styrene-*co*-vinylbenzophenone) with increasing ratio of benzoyl chloride to phenyl groups in polystyrene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the DSC curves were decreased as the grafting rates of benzophenone chromophoric groups in the resultant polymers increased up to the ratio of benzoyl chloride to phenyl groups in polystyrene, 1 : 1 [Fig. 6(c)]. It was assumed that the incorporated benzophenone chromophoric side group in the main polymer backbone widened the space between the adjacent main polymer chains in the poly (styrene-*co*-vinylbenzophenone) and so the Van der Waals' forces between adjacent main polymer chains were decreased. However, above the ratio of 2 : 1, the pattern of DSC curves was totally different from that of pristine polystyrene. In general, atatic polystyrene
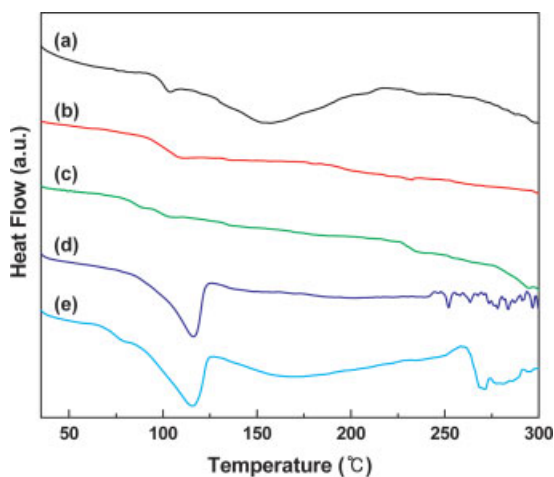
used in this study is a 100% amorphous polymer, so no significant melting point (T_m) and crystallization temperature (T_c) were observed in DSC.[16] However, a new significant endothermal peak was observed in the DSC curves of poly (styrene-*co*-vinylbenzophenone) copolymers at temperatures higher than the glass temperature (T_g) of pure polystyrene when the ratio of benzophenone chloride to phenyl groups in polystyrene was above 2 : 1. It was assumed that the incorporation of polar benzophenone chromophoric side chains in polystyrene could enhance dipole–dipole intermolecular and intramolecular interactions, which would form some new crystal domain in the poly (styrene-*co*-vinylbenzophenone). Similarly, T_g values of the copolymers were overall higher than that of pristine polystyrene, which is the evidence of the polar benzophenone chromophoric groups enhancing dipole–dipole interactions. As a result, the rigidity of the resultant polymer should be increased.[17–19]

XRD analysis was conducted to investigate whether any new crystal domain was created in the poly (styrene-*co*-vinylbenzophenone) with high benzophenone contents. Figure 7 shows the XRD scans of polystyrene, poly (styrene-*co*-vinylbenzophenone) with the ratios of benzoyl chloride to phenyl groups in polystyrene as 2 : 1 and 1 : 1, respectively. The peak of polystyrene at 2θ = 19.5°, the most intense one in the XRD scan of polystyrene, is amorphous peak corresponding to Van der Waals distance. In polystyrene, the main polymer chains are approximately parallel to one another leading to a distance between adjacent chains.[20] On the other hand, in the XRD patterns of poly (styrene-*co*-vinylbenzophenone), the peak intensity at around 2θ = 19.5°

Figure 6 DSC thermograms of pristine polystyrene (a) and poly (styrene-*co*-vinylbenzophenone) with various ratios of benzoyl chloride to phenyl groups in polystyrene as 0.5 : 1 (b), 1 : 1 (c), 2 : 1 (d), and 4 : 1 (e). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
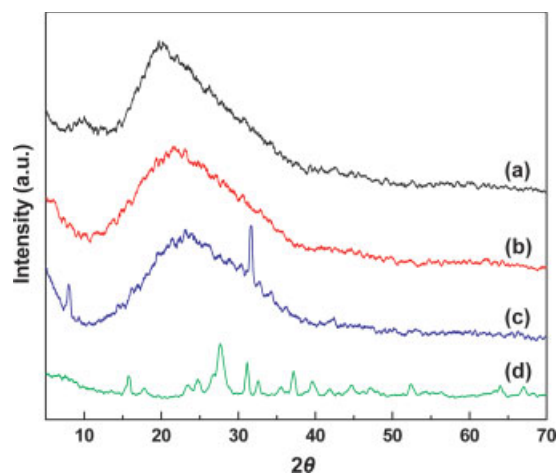

Figure 7 XRD scans of pristine polystyrene (a), poly (styrene-*co*-vinylbenzophenone) with ratios of benzoyl chloride to phenyl groups in polystyrene as 1 : 1 (b) and 2 : 1 (c), and AlCl$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Colony Numbers of *S. aureus* after Injection of 0.1-mL Bacteria Suspension
on Agar Plates and Incubation at 37°C for 18 h

Against to *S. aureus*	Dilution ratio of the bacteria solution after contact time				Reduction of bacteria (%)
	$\times 10$	$\times 10^2$	$\times 10^3$	$\times 10^4$	
Pristine polystyrene	∞	∞	77	24	–
Poly(styrene-*co*-vinylbenzophenone) 0.5 : 1	∞	∞	21	9	62.50
Poly(styrene-*co*-vinylbenzophenone) 1 : 1	3	0	0	0	>99.99
Poly(styrene-*co*-vinylbenzophenone) 2 : 1	0	0	0	0	>99.9999
Poly (styrene-*co*-vinylbenzophenone) 4 : 1	0	0	0	0	>99.9999

decreased with increasing the content of benzophenone groups, possibly due to the widened space between the adjacent main polymer chains caused by the incorporated benzophenone side groups in the copolymer main chains. Besides, it was observed that a long range order peak at $2\theta \sim 8°$ and a new higher field peak at $2\theta \sim 31.5°$ appeared in one curve of poly (styrene-*co*-vinylbenzophenone) copolymer [Fig. 7(c)], and the crystallinity of the copolymer was about 4.16%.[21] The long range order peak at $2\theta \sim 8°$ could be from new crystal domains in the copolymer. The new peak at $2\theta \sim 31.5°$ should not be from residual AlCl₃, because $2\theta \sim 31°$ peak was observed but the $2\theta \sim 8°$ peak was not observed in the AlCl₃ curve [Fig. 7(d)]. Despite the fact that AlCl₃ is a Lewis acid, it was well known that due to the electron-withdrawing effect of the carbonyl group, the aromatic ketone group is always less reactive than the aliphatic ones, so multiple acylations could not occur on phenyl rings. Also, there is no carbocation rearrangement, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen.[22,23] However, it was observed that at the ratio of benzoyl chloride to phenyl groups in polystyrene equals 2 : 1, the resulted poly (styrene-*co*-vinylbenzophenone) was unable to form films with smooth surface.

Antibacterial abilities of copolymers

Tables I and II show the antibacterial results of the poly (styrene-*co*-vinylbenzophenone) copolymers

against *S. aureus* and *E. coli*, respectively. The numbers of colonies of *S. aureus* and *E. coli* were significantly reduced as the content of benzoyl chloride increased in the acylation reactions. Particularly, when the ratio of benzoyl chloride to phenyl groups in polystyrene was at or above 2 : 1, the poly (styrene-*co*-vinylbenzophenone) copolymers provided 99.9999% bacterial reduction against both *E. coli* and *S. aureus* in a contact time of 1 h. When the ratio of benzoyl chloride to phenyl groups in polystyrene was reduced to 1 : 1, the poly (styrene-*co*-vinylbenzophenone) copolymer still showed excellent antibacterial ability (>99.99% against *S. aureus* and >99.999% against *E. coli*). Although even when the ratio of benzoyl chloride to phenyl groups in polystyrene was increased to 4 : 1, the unreacted phenyl groups can still be observed in NMR [Fig. 4(c)]. It seems that at a ratio of 1 : 1 the resultant polymer could contain sufficient photo active benzophenone groups to provide desired antibacterial functions effectively.

Based on the superior photo-activated antibacterial performance, these copolymers could find applications as topical coating or surface active materials in food packaging products, medical devices and hygienic goods.

CONCLUSIONS

Polymers containing benzophenone chromophoric groups were successfully prepared by a simple Friedel-Crafts acylation of polystyrene with benzoyl chloride. The incorporated amount of benzophenone

TABLE II
Colony Numbers of *E. coli* after Injection of 0.1-mL Bacteria Suspension
on Agar Plates and Incubation at 37°C for 18 h

Against to *E. coli*	Dilution ratio of the bacteria solution after contact time				Reduction of bacteria (%)
	$\times 10$	$\times 10^2$	$\times 10^3$	$\times 10^4$	
Pristine polystyrene	∞	∞	∞	85	–
Poly(styrene-*co*-vinylbenzophenone) 0.5 : 1	∞	∞	∞	48	43.53
Poly(styrene-*co*-vinylbenzophenone) 1 : 1	10	1	0	0	>99.999
Poly(styrene-*co*-vinylbenzophenone) 2 : 1	0	0	0	0	>99.9999
Poly(styrene-*co*-vinylbenzophenone) 4 : 1	0	0	0	0	>99.9999

chromophoric groups in the resultant poly (styrene-*co*-vinylbenzophenone) increased as the content of benzoyl chloride in the acylation bath was increased. And the copolymers containing more benzophenone groups showed enhanced photoactivities and consequently better antibacterial abilities. However, when the content of benzophenone groups was increased too high, the resultant poly (styrene-*co*-vinylbenzophenone) was unable to form films with smooth surface. The poly (styrene-*co*-vinylbenzophenone) prepared at a ratio of 1 : 1 of benzophenone chloride to phenyl groups in polystyrene was able to provide adequate antibacterial functions and still maintain acceptable mechanical properties.

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