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Polymer 46 (2005) 10883–10889

polymer

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Preparation and characterization of PbS nanoclusters made by using a powder method on ionomers

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Received 2 June 2005; received in revised form 5 August 2005; accepted 30 August 2005
Available online 22 September 2005

Abstract

By using a powder method, a new method for producing semiconductor/polymer nanocomposites, lead sulfide (PbS) nanoparticles were prepared and dispersed in either poly(methylmethacrylate-*co*-methacrylic acid) or poly(styrene-*co*-styrenesulfonic acid). The size of the nanoclusters was less than 2 nm, and the size distribution was rather sharp, determined by UV–vis absorption spectroscopy. The absorption spectra of the PbS-containing sheets showed a blue shift and the absorption edges were steep, reflecting the formation of nano-sized PbS clusters. The spectra also exhibited an absorption maximum, which is an indication of a narrow particle size distribution. The glass transition temperature (T_g) of the PbS-containing nanocomposites was higher than that of the corresponding ionomer. The effect of heat treatment on the aggregation of PbS is also discussed. The dissolution of powder samples, followed by neutralization of acidic groups, led to reduction of particle sizes, suggesting the usefulness of ionic groups for stabilizing PbS nanoclusters.

Keywords: PbS nanoclusters; Powder method; Ionomers

1. Introduction

Semiconductor nanoclusters, ranging in diameter between 1 and 10 nm, have been the subject of intense investigation in recent years [1–6]. Due to their extremely small size and large specific surface area, nanoclusters exhibit electronic and optical properties that are different from those of bulk semiconductors. For a semiconductor crystal, electronic excitation consists of a loosely bound electron–hole pair (i.e. exciton), usually delocalized over a length much longer than the lattice constant. As the size of the small semiconductor crystals (i.e. crystallites) is reduced to the exciton Bohr radius, its electronic properties begin to change, a phenomenon referred to as the quantum size (confinement) effect [5].

If the crystallite sizes are below the exciton Bohr radius in the semiconductor, strong quantum confinement occurs. The confinement effect appears as a shift to lower wavelengths in the absorption spectrum (a blue shift), which reflects a change in the band gap. The absorption shift and spectral features can be a measure of particle size and size distribution. Thus, one can prepare white cadmium sulfide (CdS) instead of orange bulk CdS, and yellow–brown lead sulfide (PbS) instead of black bulk PbS. For PbS, the strong quantum confinement effect can be observed for a cluster as large as 20 nm. PbS has a bulk absorption edge at 3200 nm, which can be decreased to 530 nm for very small clusters due to the quantum confinement effect [7]. PbS also exhibits a high dielectric constant and a large exciton Bohr radius (18 nm) [8]. Since, large particles are thermodynamically more stable than smaller particles are, preparation of kinetically stable (frozen) semiconductor clusters in a proper media is desirable for various applications. PbS particles have been prepared in various media, including organic solutions [9,10], zeolites [11], glasses [12] and ionomer films [7,13–16].

Ionomers are ion-containing polymers (usually having ionic groups of less than 15 mol%) whose bulk properties are governed by ionic interactions [17,18]. These ionic interactions result in the formation of nm-sized ionic aggregates, and in random ionomers, there is a statistical distribution of ionic units along the polymer chains. Eisenberg and co-workers have demonstrated that it is possible to control aggregate sizes in random ionomers by varying the structure of the ionic units [15,19]. Because nm-sized ionic aggregates are formed in ionomers, ionomers have been used as a template to produce semiconductor nanoclusters [7,15]. These studies have used ionomer films that contain metal counterions (e.g. Pb^{2+}),

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doi:10.1016/j.polymer.2005.08.084

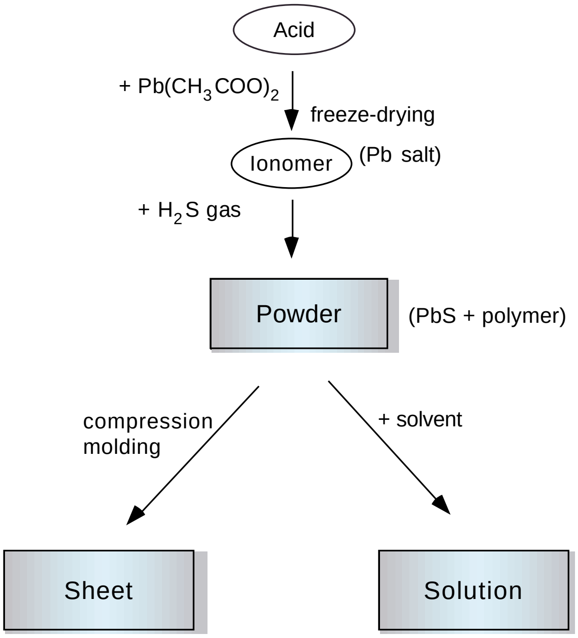

Fig. 1. A schematic figure showing the power method for the preparation of PbS nanoparticles by using ionomers.

and after passing H_2S gas, metal ions are converted to PbS particles of nanometer scale. Although interesting, only film specimens can be made and bulk materials cannot be easily made by using such a method (a film method).

In this paper, we report the preparation of PbS semiconductor nanoclusters in the polymer matrix via a new method (a powder method) by using ionomers (Fig. 1). In this method, we can prepare powder samples that contain PbS-nanoclusters from freeze-dried Pb-salt ionomers. The powder samples can be used directly. Also, these powder samples can further be processed to form bulk (sheet) materials or dissolved in a solvent that does not dissolve PbS. In addition, due to the stabilizing effect provided by the functional groups of polymers, aggregation can be minimized and nanoclusters can be formed despite a thermal process involved. We have determined the size of PbS nanoclusters by using X-ray diffraction for larger clusters (>2 nm) and UV–vis spectroscopy for smaller clusters (<2 nm). The solution behavior of these systems was also investigated by conductometric titrations.

2. Experimental

2.1. Materials

Poly(methyl methacrylate-*co*-methacrylic acid) (MMA-6.0%MAA) was purchased from Polyscience Inc. and poly(styrene-*co*-styrenesulfonic acid) (S-5.3%SSA) was synthesized in this laboratory. Here, 6.0%MAA and 5.3%SSA mean 6.0 mol% of MAA residues and 5.3 mol% of SSA residues, respectively. The preparation and characterization of these polymers were reported elsewhere [20,21]. All solvents were ACS grade and used as received.

2.2. Preparation of MMA-6.0%MAA-Pb ionomer

Acid sample, MMA-6.0%MAA, was dissolved in benzene/methanol (90/10:v/v) mixture in a round bottom flask. After dissolution of the polymer, lead acetate ($Pb(CH_3COO)_2$) dissolved in methanol was added drop-wise. The clear solution was allowed to stir for 1 day at room temperature. The solution was then poured slowly into a large volume of methanol to precipitate the ionomer (Pb salt). The white ionomer specimen was washed repeatedly in methanol, and after being redissolved in benzene/methanol, specimens were freeze-dried.

2.3. Reaction with hydrogen sulfide (H_2S) gas: preparation of MMA-6.0%MAA/PbS

The freeze-dried white ionomer powder was reacted with H_2S gas (Aldrich). MMA-6.0%MAA-Pb ionomer sample was placed in a Claisen flask that was fitted with a gas inlet and an outlet. The outlet was connected to a balloon to maintain the flask under a positive H_2S blanket. The Pb-containing ionomer was maintained under a positive gas blanket for 1 day during which the color changed from pure white to bright yellow–orange. To remove the excess H_2S, the flask was opened to atmosphere in a well-ventilated fume hood for about 3 h. Further removal of the gas was carried out in a vacuum oven at room temperature for another 12 h. The reaction is shown schematically in Fig. 2.

2.4. Reaction with anhydrous ammonia gas

With the intent to convert the $-COOH$ groups to $-COO^-NH_4^+$, some of the H_2S-treated yellow–orange ionomer was reacted with anhydrous ammonia gas (Aldrich) by following the same procedure as described for H_2S gas treatment. During this reaction no appreciable change in color was observed.

2.5. S-5.3%SSA samples

Poly(styrene-*co*-styrenesulfonic acid) with an acid content of 5.3 mol% (S-5.3%SSA) was reacted with lead acetate and worked up further by using the same procedures as those described for the MMA-6.0%MAA system.

2.6. Compression molding

Sheet specimens were prepared by melt pressing in a compression molding machine (Waback). Dry polymer sample was placed between a Teflon coated aluminum foil (McMaster Carr Supplies Co.) and melt pressed between two preheated flat metal plates. The molding temperature and pressure were 180 °C and 2000 psi, respectively. The molding time was 5 min and the mold was air cooled to about 100 °C and then by cold water to room temperature.

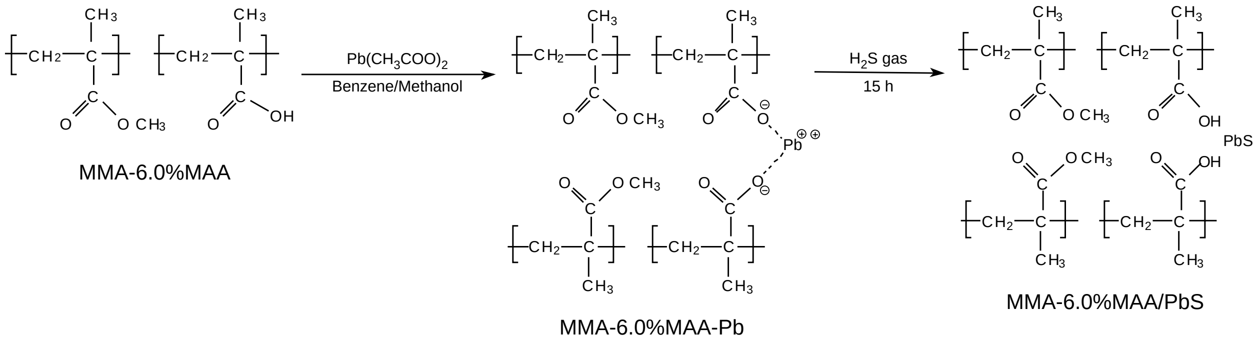

Fig. 2. Reaction involved in forming PbS-nanoclusters by using PMMA ionomers.

2.7. Modulated differential scanning calorimetry (MDSC)

MDSC measurements were conducted on small specimens that were made by cutting the compression molded samples. Measurements were performed on a TA instrument MDSC 2910, at a heating rate of 10 °C/min and a temperature oscillation of ±1.5 °C/40 s. Highly purified nitrogen gas was used for purging at a flow rate of 70 ml/min. The sample weight was about 10 mg. The first scan was excluded and the second and third scans were used for analysis. The glass transition was defined as the inflection point of the transition.

2.8. X-ray diffraction

X-ray diffraction measurements for sheet specimens were conducted with X-ray diffractometer (Siemens D5000) for which Cu K_α (1.54 Å) was used. A quartz zero background holder was used to place sheet specimen.

2.9. Ultraviolet–visible (UV–vis) light absorption spectroscopy

UV–vis absorption spectra were recorded on a microtec scanning plate spectrophotometer (Biotek Instruments). All the ionomer film samples were scanned between 200 and 800 nm in wavelength.

2.10. Conductometric titration

The electrical conductivity of the PbS-containing ionomer samples were studied in benzene/methanol solvent mixture by using an Accumet model 20 pH/conductivity meter. A cell assembly had platinum electrodes of cell constant of $0.99\ \mathrm{cm}^{-1}$. A microsyringe was used to add NaOH in methanol for titration.

3. Results and discussion

3.1. Physical appearance and solubility of samples

The solubility and physical appearance of the prepared samples are given in Table 1. Freeze drying of the MAA-6.0%MAA-Pb ionomer samples resulted in white powders that were soluble in benzene/methanol mixture (90/10:v/v). By contrast, S-5.3%SSA-Pb did not show complete dissolution. Because ionic bonds act like physical cross-links and affect solubility, this indicates that the bonding between sulfonate groups and Pb^{2+} is stronger than that between carboxylate groups and Pb^{2+}. Such phenomenon is well known for ionomers containing divalent metal ions [17].

When the Pb-containing ionomers (in freeze-dried powder form) were reacted with H_2S, their color changed from pure white to dull yellow and finally bright yellow–orange. The color distribution over the samples was homogeneous, and no black particles that are seen for bulk PbS were detected. The color change qualitatively served to indicate the formation of PbS particles in ionomers. The compression molded polymer sheets containing PbS were transparent yellow for the S-5.3%SSA and transparent red for the MMA-6.0%MAA, suggesting the formation of smaller sized nanoclusters in the S-5.3%SSA matrix than in the MMA-6.0%MAA matrix. The molding time was always maintained at 5 min to minimize thermally induced aggregation of PbS particles [7].

Some of the H_2S treated samples were treated with anhydrous ammonia gas with the intent to convert the $-COOH$ groups to $-COO^-NH_4^+$. However, during the reaction no appreciable color change was noted. Both UV–vis spectroscopy and DSC did not show any differences either. This indicates little usefulness of this processing method; thus, no further studies have been made with NH_3.

Table 1
Physical appearance and solubility of ionomers and PbS nanocomposites

Ionomer	Physical appearance		Solubility in benzene/ methanol (90/10:v/v)	
	Powder	Sheet[a]	Powder	Sheet
MMA-6. 0%MAA-Pb	White[b]	Transparent colorless	Soluble	Soluble
MMA-6. 0%MAA/PbS	Yellow[c]	Transparent red	Soluble	Soluble
S-5.3%SSA-Pb	White[b]	Transparent colorless	Incomplete	Incomplete
S-5.3%SSA/PbS	Yellow[c]	Transparent yellow/ brown	Incomplete	Incomplete

[a] Made by compression molding a powder sample at 180 °C for 5 min.
[b] Made by freeze-drying.
[c] Made by treating a freeze-dried sample with H_2S gas.

Table 2
Glass transition temperatures of sheets specimens for acids, ionomers, and PbS nanocomposites

Ionomer	T_g (°C)
MMA-6.0%MAA	113.4
MMA-6.0%MAA-Pb	125.2
MMA-6.0%MAA/PbS	129.4
S-5.3%SSA	117.9
S-5.3%SSA-Pb	122.9
S-5.3%SSA/PbS	124.2

3.2. Glass transition temperatures

The glass transition temperatures of the ionomer samples are given in Table 2. The Pb-containing ionomers show an increase in T_g as compared with acid forms. This increase is due to ionic cross-linking effect of either SO_3^- or COO^- with Pb^{2+} ions. This cross-linking prevents chain mobilization and thereby raises the T_g [17,22]. The T_g values are also higher for the acid polymer with the PbS particles. This is attributed to the presence of ultra-small PbS particles in the polymer matrix. An increase in T_g with the addition of very small particles was reported by Cousin and Smith [23]: the T_g of sulfonated polystyrene is increased with the addition of Al_2O_3 (10 nm) as a result of interactions between SO_3H groups of the polymer and the groups of the particles, which may introduce additional cross-linking effect on the ionomer chains. By contrast, neutral polymers containing very small particles do not show an increase in T_g, e.g. polystyrene or PMMA with SiO_2 (7 nm) [24]. No second higher T_g was observed for all the samples studied in this work. This may be due to the lower sensitivity of DSC to the small second phase (as compared with dynamic mechanical thermal analysis) [18] and to rather low ion contents of the samples used, since the higher T_g reflects the presence of ionic clusters which begin to dominate at a critical ion content: ca. 6 mol% for PS ionomers [17] and ca. 12 mol% for PMMA ionomers [20]. All the samples decomposed at ca. 210 °C, as studied by DSC measurements. Visual observation of the samples indicated that they became dark brown and very brittle.

3.3. Effect of heat treatment on the size of PbS nanoclusters determined by X-ray diffraction

In the beginning of this work, we used X-ray diffraction to study the effect of heat treatment on the size of PbS particles. Since, the particle size increased when heat treatment was applied for prolonged time, the effect of heat treatment on the aggregation of PbS nanoclusters in S-5.3%-SSA was studied. The same observation applied to PbS nanoclusters in MMA-6.0%MAA.

Fig. 3 shows the X-ray diffraction spectra of the solvent cast films before and after heat treatment as well as that of an ionomer precursor (acid sample). Also, X-ray data of a film of similar thickness made by compression molding (at 220 °C for 2 h) is shown in Fig. 3 for comparison. It is clear that the PbS-containing film (made by solvent casting) does not exhibit a diffraction peak because of the formation of extremely small PbS particles. The same film after heating under vacuum at 150 °C for 3 h showed a peak at a diffraction angle ($2\theta_B$) of 43.25°. The diffraction curve is consistent with that of nano-sized PbS crystals, which retain the diffraction pattern of a bulk PbS cubic rock-salt structure [7]. The average particle size, D, from the line width was determined by using Scherrer's equation [25]

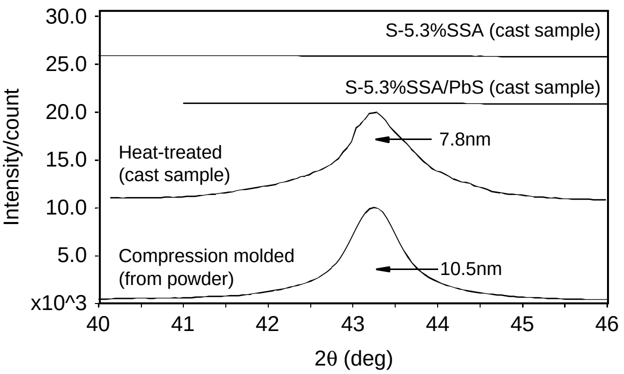

Fig. 3. X-ray diffraction spectra of S-5.3%SSA-H (acid), S-5.3%SSA/PbS (cast from solvent), S-5.3%SSA/PbS (after heat-treatment of a cast film), and S-5.3%SSA/PbS (compression molded film from powder).

$$D = \frac{\lambda_X}{B \cos \theta_B} \tag{1}$$

where B is the (angular) half-width of the diffraction peak (at $2\theta_B$) and λ_X is the wavelength of X-ray (1.542 Å). According to Eq. (1), the line-width broadens with a decrease in the particle size. The particle size of the cast film after heating is 7.8 nm, while that prepared by compression molding is 10.5 nm. By considering the higher temperature used for compression-molded samples (220 °C) than that for heated cast samples (150 °C), the effect of heat treatment is essentially comparable for both samples. Note that the compression molded samples used here were thinner than those usually made in this work, and were heated much longer at higher temperature here (for 2 h at 220 °C) than usual (for 5 min at 180 °C); thus, leading to the formation of rather large aggregates of PbS particles.

3.4. PbS nanocluster sizes and size distributions determined by UV–vis absorption spectroscopy

According to the heat treatment study described above, we have decided to make sheet specimens by compression molding at 180 °C for 5 min to minimize aggregation. Since, the size of clusters smaller than 2.5 nm cannot be reasonably determined by the X-ray diffraction method [7], as is the case for the PbS nanoclusters made by compression molding (for 5 min) in this work, UV–vis absorption spectroscopy has been used to determine the size of nanoclusters.

The absorption edge (λ_e), obtained from the intersection of the sharply decreasing region of the spectrum with the baseline, is blue shifted when the size of semiconductor nanoclusters is decreased [7,14]. The UV–vis absorption spectra of compression-molded sheet specimens are shown in Figs. 4 and 5.

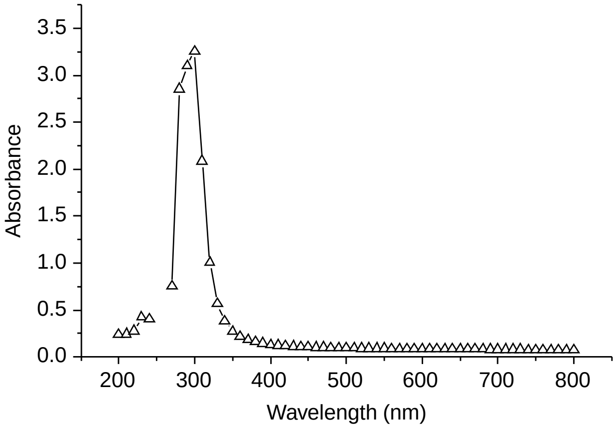

Fig. 4. UV–vis absorption spectrum of PbS nanoclusters in S-5.3%SSA (after subtracting the spectrum of S-5.3%SSA).

Since the absorption edges of the PbS-containing polymers were greatly blue-shifted from the value of bulk PbS (3200 nm), and since the absorption edge of quantum confined PbS clusters is known to be at lower wavelengths than that of the bulk PbS [7], our data indicate the formation of PbS nanoclusters. The slope of the absorption spectra is also steep, another indication of the formation of small PbS clusters. An absorption maximum or an exciton maximum (λ_m), reflects a relatively narrow size distribution of clusters [4]. Other than the distinct absorption maximum the spectra are featureless. The absence of other excitonic structure may be attributed to weak exciton binding energy due to strong Coulomb screening. Similar featureless spectra were reported for PbS particles formed in poly(vinyl butyral) films [26]. Another reason for the non-existence of other excitonic peaks could be due to the capping of PbS particles by either $-$COOH or SO_3H groups of the polymers [27].

The correlation between absorption edge values and PbS particle diameters was made by Moffitt and Eisenberg [15] using a theoretical model developed by Wang et al. [7]: $2R = \exp(0.9587 + 0.09468\lambda^{1/2})$, where R is the radius and λ is the absorption wavelength. The sizes of the PbS particles determined by this relation are listed in Table 3. The diameter values, 1.8 nm in MMA-6.0%MAA and 1.5 nm in S-5.3%SSA, are within the range of quantum confinement (less than 18 nm). A useful measure of polydispersity of the sample is obtained by determining the half-width of size distributions (number of particles vs. particle diameter), $d_{1/2}$. The $d_{1/2}$ is determined by

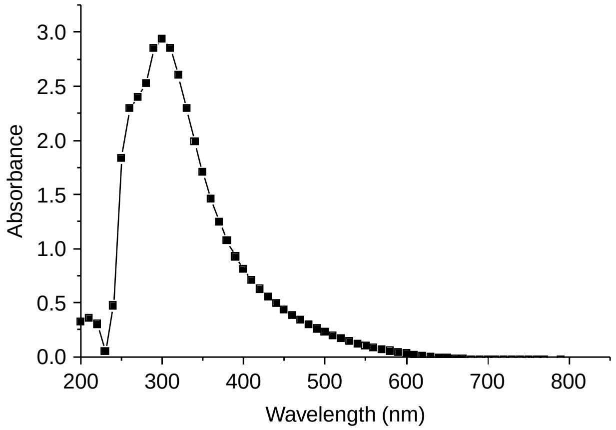

Fig. 5. UV–vis absorption spectrum of PbS nanoclusters in MMA-6.0%MAA (after subtracting the spectrum of the MMA-6.0%MAA).

Table 3
Size and distribution of PbS nanoparticles in ionomer sheets determined by UV–vis absorption spectra

Ionomer	λ_{max} (nm)	λ_e (nm)	$2R_{PbS}$ (λ_m) (nm)	$2R_{PbS}$ (λ_e) (nm)	$d_{1/2}$ (nm)	RPI
MMA-6.0%MAA/PbS	290	421	1.31	1.82	0.51	1.04
S-5.3%SSA/PbS	302	346	1.35	1.52	0.17	1.004

$$d_{1/2} = 2R_{PbS}(\lambda_e) - 2R_{PbS}(\lambda_m) \quad (2)$$

where $R_{pbs}(\lambda_e)$ and $R_{pbs}(\lambda_m)$ are radii of PbS nanoparticles from an absorption edge and an absorption maximum, respectively. It has been shown that the smaller the $d_{1/2}$ value, the closer to monodisperse the particles are [28]. The determined $d_{1/2}$ values given in Table 3, 0.51 nm in MMA-6.0%MAA and 0.17 nm in S-5.3%SSA, indicate a narrow size distribution of PbS particles. If we assume a Gaussian distribution of particles (in the number of particles vs. diameter curves), $d_{1/2}$ values can be taken to be twice the standard deviation (σ_{2R}), and $2R_{PbS}(\lambda_m)$ will approximate the mean particle diameter. Using this approximation a radius polydispersity index (RPI) is defined for each distribution by the following equation [16].

$$\mathrm{RPI} = \left[\frac{\sigma_{2R}}{2R_{PbS}(\lambda_m)}\right]^2 + 1 \quad (3)$$

It can be seen from Table 3 that the RPI values determined for PbS clusters prepared in compression-molded sheets are close to 1.0. This low value indicates a narrow distribution of PbS particles in the ionomer matrix and is in good agreement with the reported result [16]. However, as pointed out by Moffitt et al., the assumption of a Gaussian distribution may not be realistic and therefore the RPI values are approximate values [16]. It should be stressed that the sizes of PbS nanoclusters obtained by our method (a powder method) are close to those obtained by a film method [15]. Since, the film method does not involve heating, this suggests that compression molding of powder samples for a short time (5 min) does not induce aggregation of nanoparticles and allow to make 3D samples. This is indeed one of the advantages of our method.

3.5. Solution samples titrated with NaOH

The PbS-containing ionomer powders, MMA-6.0%MAA/PbS, were soluble in benzene/methanol solvent mixture (90/10:v/v) resulting in clear orange solutions. In Fig. 6, a bottle A corresponds to MMA-6.0%MAA/PbS dissolved in a benzene/methanol solvent mixture. The solution remained optically clear even after 15 days of preparation (see

Fig. 6. Photograph of solution samples in benzene/methanol mixture: (A) MMA-6.0%MAA/PbS (1 day); (B) untitrated MMA-6.0%MAA/PbS (15 days); (C) titrated MMA-6.0%MAA/PbS; (D) usual bulk PbS powder.

a bottle B). When this solution was titrated (neutralized) with 0.1 N NaOH in methanol, the color of the solution gradually turned less intense and turned yellow from orange (see a bottle C) and no precipitation of the sample was observed. Note the precipitated (insoluble) black PbS sample when bulk macro-sized PbS powder was simply mixed with the solvent (see a bottle D). The color change may reflect the reduction of the size of PbS nanoclusters. Upon titration, acid ($-$COOH) groups of the polymer are converted to ionic ($-COO^-Na^+$) groups which can further stabilize the PbS nanoparticles, thereby bringing about the change in color of the solution.

Fig. 7 shows the result of conductometric titration of the MMA-6.0%MAA/PbS sample with methanolic NaOH in benzene/methanol. The conductance value is nearly zero before titration, since no ions exist in this solution. Upon titration of $-$COOH groups, $-COO^-Na^+$ ion pairs are formed, which also have little contribution to conductance in this solvent. After all the $-$COOH groups are titrated (neutralized), additional NaOH added to the solution produces Na^+ and OH^- ions in solution, which have significant contribution to conductance, leading to a sharp rise in conductance, as seen in Fig. 7 [29]. The titration curve was smooth exhibiting a clear end point that corresponds to an ion content of 5.9 mol%, which is close to the value of acid content of the parent polymer (6.0 mol%). This clearly indicates that all the $-$COOH groups are converted to $-COO^-Na^+$ ion pairs. We can speculate that the color change observed during the titration is attributed to the conversion of the acidic groups to ionic groups, followed by stabilization of the PbS particles by the ionic groups. Although the exact nature of the bonding between ionic groups and PbS particles is not clear, it is nevertheless expected that ionic groups can interact more favorably with PbS than nonionic groups can, and this leads to a stabilizing effect.

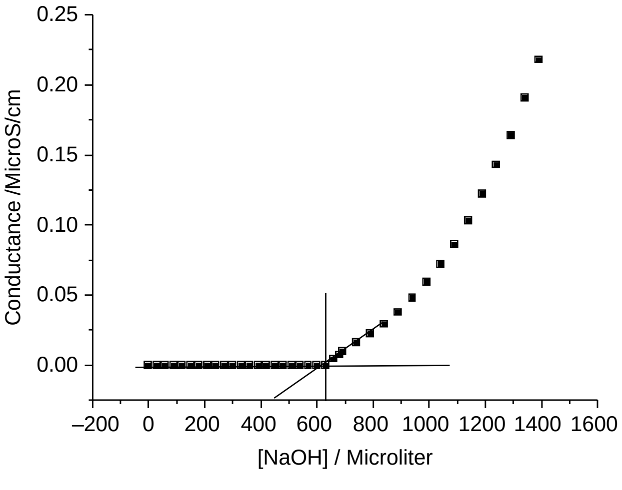

Fig. 7. Conductance of MMA-6.0%MAA/PbS solution in benzene/methanol (90/10:v/v) titrated with methanolic NaOH solution.

If this argument is valid, the absorption spectrum of the solution should show a blue shift. Fig. 8 shows the spectra of the MMA-6.0%MAA/PbS solution before and after titration (both after subtracting the spectrum of the acid polymer solution). As expected, a clear blue shift of the absorption edge was observed for the titrated solution. This clearly shows that the size of the PbS particles has indeed reduced and stabilized by the presence of ionic groups. The untitrated sample does not show any excitonic features, whereas the titrated sample seems to show a weak excitonic feature at around 410 nm. Although a peak is very small, this seems similar to a weak peak observed for PbS nanoparticles, which is attributed to $1_{s_e} - 1_{p_h}$ electronic transition [26,30]. Watzke and Fendler have also reported that small CdS particles can be prepared in the presence of electrolytes [28].

This result may offer a simple method for preparing organic-soluble PbS nanoparticles that are stabilized by ionic groups. Interestingly, bulk PbS is not soluble in any organic solvent but is only soluble in hot hydrochloric acid or nitric acid. It is neither soluble in water nor does it shows any reactions with water, and therefore any possible side reactions are excluded.

3.6. A powder method vs. a film method

We have shown that a powder method is useful to produce PbS nanoclusters in the polymer matrix. First, due to freeze-drying, PbS nanocomposites are formed as porous powder samples, which can be used directly. Second, by compressing molding (for 5 min), 3D samples can be made, where aggregation is minimized. This is not easily achieved by the film method. Third, powder sample can easily be dissolved in the organic solvent that cannot dissolve PbS, forming solution sample that contains nanoclusters. This is made possible due to the soluble polymer molecules surrounding PbS nanoclusters. In solid samples (in either powder or sheet), nanoclusters are surrounded and protected by functional groups (acid groups) of polymer molecules. Although we intended to use ionic groups as functional groups, our method as well as the film methods [7,15,16] end up with acid functionalities to stabilize nanoclusters in solid state. We have succeeded this in solution. The conversion to ionic groups and their use as a stabilizer of nanoclusters in the solid state is the subject of future work.

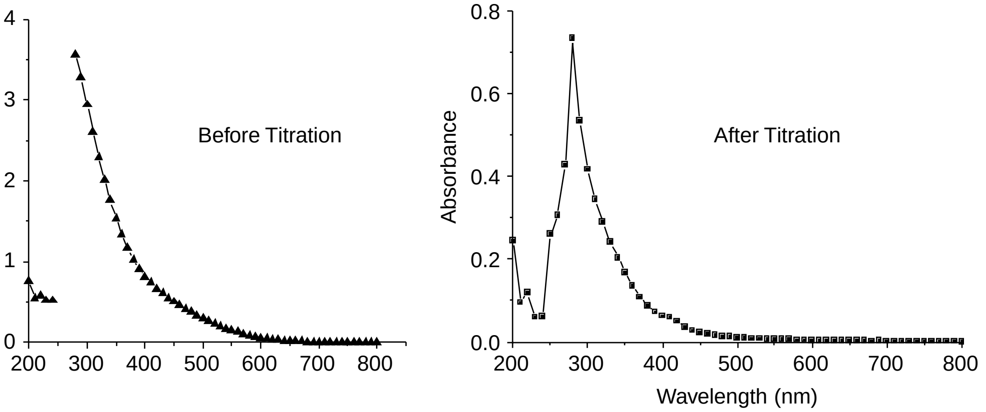

Fig. 8. UV–vis absorption spectra of MMA-6.0%MAA/PbS solution before and after titration with 0.1 N NaOH (after subtracting the spectrum of the MMA-6.0%MAA solution).

4. Conclusions

By using a powder method, ionomer powder samples that contain well-dispersed PbS nanoclusters were successfully prepared. In addition to the direct use of a powder sample, this powder can further be processed to form a 3D sheet sample (i.e. thermoplastic) or be dissolved in a solvent to form a solution sample. The size of the nanoclusters in the sheet samples is less than 2 nm and the size distribution is very narrow, which is reflected in the calculated $d_{1/2}$ values as well as the sharp absorption maximum. Although prolonged heating (over 2 h) caused the nanoparticles to agglomerate (to the size of 10 nm), usual processing time (5 min) minimizes such agglomeration. The reaction of ammonia gas with the H_2S reacted samples did not show any significant effect in the solid state, which could be due to the weak basic nature of the gas. The PbS-containing (PMMA-based) polymer samples were completely soluble in a solvent mixture (benzene/methanol) and did not show any precipitation on storage even for 2 months. The PbS nanoclusters were further stabilized by titration (neutralization) with sodium hydroxide, demonstrating thereby the usefulness of ionic groups in stabilizing nanoclusters. This work has demonstrated the usefulness of a powder method for the preparation of quantum confined PbS particles in the polymer matrix both in the solid state and in solution. This is the first part of our work on nanocomposites by using the powder method on ionomers. Various properties of these composites and their relationships with structures will be reported in the future.

Acknowledgements

The authors thank Dr William E. Mayo for obtaining X-ray diffraction data and the Rutgers Research Council for financial support of this work.

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