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Synthesis and Properties of Polystyrene Carrying Pendant Hydroxybarbiturate Groups

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The preparation and properties of barbiturate- and thiobarbiturate- functionalized polystyrenes [(BAPS) & (TBAPS)] synthesized by the chemical modification of polystyrene homopolymer are discussed. The fluorescence emissions of the polymers are found to be dependent on the nature of the substituent, as well as its concentration and this is estimated as well. Fluorescence microscopic studies of BAPS and TBAPS in water indicated the formation of polymeric aggregates in a solution of about 5 μm. Surface tension measurements confirmed the formation of aggregated structures in aqueous solution. The polymers synthesized are observed to chelate a wide variety of metal ions, the % uptake of which is observed to increase with increasing mol% of the pendant functional groups.

Keywords functional polymers, fluorescence, surface active, water-soluble polymers, association, chelation, metal ions

Introduction

The preparation and physical properties of statistical/random copolymers with a wide compositional window are a novel topic of exploratory interest.^[1] This is primarily due to the fact that control over the composition of statistical copolymers is difficult to achieve via the conventional chain growth copolymerization methods. In the widely practiced methods of copolymer synthesis the composition of the copolymer is dictated primarily by the reactivity of the propagating species, and to a certain extent, by the feed ratio of the monomers (since the feed ratio varies continuously during the progress of a copolymerization). For example, the chain copolymerization of styrene with 4-acetoxystyrene or styrene with 4-vinylpyridine results in a random copolymer with a narrow and well-defined composition. The development of an alternate method of varying the composition of pendant functional groups in a given homopolymer backbone towards the objective of investigating the variation of several properties such as fluorescence, side-chain liquid crystallinity and polymer association in solution is thus a challenging area of research.

In the case of homopolymers such as polystyrene, the simpler way of introducing liquid crystalline behavior is by the introduction of structural units capable of effecting

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liquid crystalline behavior in styrene monomer and then polymerizing it suitably later.^[2] This method has a serious limitation in that the liquid crystalline behavior cannot be tailored by the variation of the composition of the group responsible for the behavior. Liquid crystalline behaviors have also been introduced by post polymerization modification of acrylate/methacrylate homo polymers and block copolymers and especially the synthesis of polymers with photosensitive mesoionic groups is well established.^[3–5] This method has the inherent advantage that the composition of the functional group responsible for a certain property can be varied in a controlled manner resulting in the required degree of that property. Given the fact that very small post polymer modification introduces polymer-polymer blending as observed earlier,^[6,7] the introduction of groups capable of directional bonding in a purely amorphous polymer by polymer modification in a controlled manner is significant.

In the recent past, we have reported the utility of polymer modification reactions as a unique method of preparing copolymers of styrene and a functional monomer of styrene with functional groups such as hydroxy [poly(4-vinyl phenol-co-styrene)],^[8] diethyl oxomalonate [poly(4-(diethyl oxomalonatostyrene)-co-styrene)],^[9] barbituric and thiobarbituric acid at the fourth position of the styrene repeat unit,^[10] with wide compositional variation by a simple control of stoichiometry. The introduction of desired concentration/extent of water-soluble pendant groups in a predominantly hydrophobic polystyrene promises to be exciting towards the achievement of a wide variation of physical properties of the resulting polymers.^[11,12] Therefore, investigations pertaining to the variation in fluorescence, aggregation in solution, and molecular aggregation as a function of compositional variation of the hydroxybarbiturate (BA) and hydroxythiobarbiturate (TBA) moieties introduced as pendant groups on the polystyrene backbone were studied. The results from these studies are reported in this paper.

Experimental

Materials and Methods

All the solvents and chemicals were reagent grade (SRL Chemicals, Chennai, India) and unless specified were used as received. Polystyrene (PS) (Beekay Plastics, Chennai, India; $M_n = 77600$; PDI = 3.8) was dissolved in tetrahydrofuran (THF) and was re-precipitated using excess methanol. Dichloromethane (DCM; Dan Campbell, Chennai, India), used in the acylation was dried over anhydrous CaCl_2 (Fluka, Chennai, India) and was distilled over anhydrous P_2O_5 (Fluka, Chennai, India) before use. Diethyl oxomalonate (Lancaster, Chennai, India) and anhydrous stannic chloride (Fluka, Chennai, India) were used as received. THF (Dan Campbell, Chennai, India) was freshly distilled over sodium-benzophenone just before use. Sodium methoxide, urea, and thiourea (Chimique Lab(I), Chennai, India), and concentrated HCl (Qualigens, Chennai, India), were used as received.

A Waters GPC system (New Jersey, U.S.A.; with styragel columns HR3, HR4, HR5), along with a Millennium v 2.15 data analyses package was used for the determination of number average molecular weight (M_n) and polydispersity index (PDI). Jasco FT-IR 410 (JASCO, Singapore) infrared spectrometer was used for recording IR spectra. A Jasco UV-530 (JASCO, Singapore) spectrophotometer was used for recording UV spectra. A JEOL GSX 400 (400 MHz for proton) NMR spectrometer (JEOL, Singapore) was used to record ^1H spectra. Mettler-Toledo's TGA/SDTA 851^c thermal analysis system (Schwerzenbach, Switzerland) was used to perform thermo gravimetric analysis (TGA). Surface tension

studies were carried out with a homemade Guoy surface tensiometer. Varian atomic absorption spectrometer Spectra AA-20 (Walnut Creek, California) was used for determining the concentration of metal ions.

Synthesis of Poly(4-diethyl oxomalonatostyrene)-DPS

DPS was synthesized as previously reported by us.^[9] DPS of various mole fractions of the diethyl oxomalonate moiety was synthesized by varying the stoichiometry of diethyl oxomalonate.

Synthesis of Hydroxy Barbiturate-Functionalized Polystyrene-P(S-co-BA)

150 mg of DPS (quantitatively functionalized PS is referred to as DPS while PS, with less than quantitatively functionalized diethyl oxomalonate moiety are referred to as P(S-co-DS)) was dissolved in 5 ml of dry THF. This was added to a solution consisting of 150 mg of sodium methoxide, 150 mg of urea and 20 ml of dry methanol. The solution was stirred well for 24 h. The product was isolated by precipitation using excess THF. The product is water-soluble. The polymer obtained by the complete conversion of quantitatively functionalized DPS is referred to as BAPS and the characterization data pertaining to this polymer are: ¹H NMR (400 MHz, D₂O, ppm) δ = 1.86 (br.s. CH₃) 3.8 (br.s.), 6.2 to 7.6 (m, Ar-H) 8.45(s, N-H); IR KBr form (n, cm⁻¹) = 3424 (br.s. OH), 2928, 1634 (s, ureas cyclic six membered), 1597 (s, Ar-C=C), 1438, 1100(C-O-C), 1367 (C-N) 1181, 1020. UV = 272 (weak), 230 (medium), 190 (sharp). P(S-co-HBA) of desired mole fraction of the hydroxybarbiturate moiety was synthesized by using P(S-co-DS) of varying composition. P(S-co-HBA) exhibits an intense violet color when placed in contact with concentrated sulphuric acid and this color disappears on treatment with water.

Synthesis of Thioarbiturate-Functionalized Polystyrene-P(S-co-TBA)

150 mg of P(S-co-DS) (of desired mole fraction of diethyl oxomalonate moiety) was dissolved in 5 ml of dry THF. This was added to a solution consisting of 150 mg of sodium methoxide, 150 mg of thiourea and 20 ml of dry methanol. The solution was stirred well for 24 h. The product was isolated by precipitation using excess THF. The product is water-soluble. The polymer obtained by the complete conversion of quantitatively functionalized DPS is referred to as TBAPS and the characterization data pertaining to this polymer are: ¹H NMR (400 MHz, D₂O, ppm) δ = 1.86 (br.s. CH₃) 3.8 (br.s.), 6.2 to 7.6 (m, Ar-H) 8.45(s, N-H); IR KBr form (n, cm⁻¹) = 3424 (br.s. OH), 2928, 1634 (s, ureas cyclic six membered), 1597 (s, Ar-C=C), 1438, 1100(C-O-C), 1367 (C-N) 1181, 1020. UV = 272 (weak), 230 (medium), 190 (sharp).

P(S-co-TBA) of desired mole fraction of the barbiturate moiety was synthesized by using P(S-co-DS) of varying composition. P(S-co-TBA) exhibits a violet color with concentrated sulphuric acid, which disappears on treatment with water.

Chelation of Metal-Ions from Aqueous Solutions using Polystyrene with Hydroxy Thiobarbiturate and Hydroxy Barbiturate Functional Groups

25 mg of the polymer (for example P(S-co-TBA) of 92 mol% TBA groups) was added to a 0.1 M aqueous solution of the metal ion. The mixture was stirred for few minutes, and after the precipitate of the metal ion-bound polymer settles down, the filtrate was analyzed by

atomic absorption/UV spectroscopy for metal ion uptake. The % uptake of metal ion was calculated using (metal ion in the bound form in ppm/concentration of the original solution in ppm) \times 100.

Results and Discussion

Preparation of Polystyrene With Various Compositions of the Hydroxybarbiturate and Hydroxythiobarbiturate P(S-Co-BA) and P(S-Co-TBA) Moieties^[10]

Hydroxybarbiturate and hydroxythiobarbiturate functionalized polystyrene (P(S-co-BA) and P(S-co-TBA)) were prepared from diethyl oxomalonate functionalized polystyrene (P(S-co-DS)) toward the objective of studying the variation of physiochemical properties as a result of varying composition of the pendant moieties. Earlier, we reported on the preparation of quantitatively functionalized PS with hydroxy barbiturate (BAPS) and hydroxy thiobarbiturate (TBAPS) moieties.^[10] Based on the method reported in our previous work, the preparation of polystyrene with various extents (mol%) of BA and TBA pendant moieties were carried out. At first, polystyrene with various extent of diethyl oxomalonate [P(S-co-DS)] pendant moieties were synthesized. This was accomplished by the reaction of PS with diethyloxomaloante while varying the reaction time. The variation in the molecular weight of the P(S-co-4-DS) (as followed by GPC as well as by ¹H NMR) was used to estimate the extent of pendant group introduced. The conversion versus molecular weight plot as obtained via GPC is shown in Fig. 1. Thus, P(S-co-DS) with different extents of diethyl oxomalonate moieties (0.2 to 0.94 mole fraction) were obtained, and these were used for the synthesis of P(S-co-BA) and P(S-co-TBA) moieties as shown in Table 1.

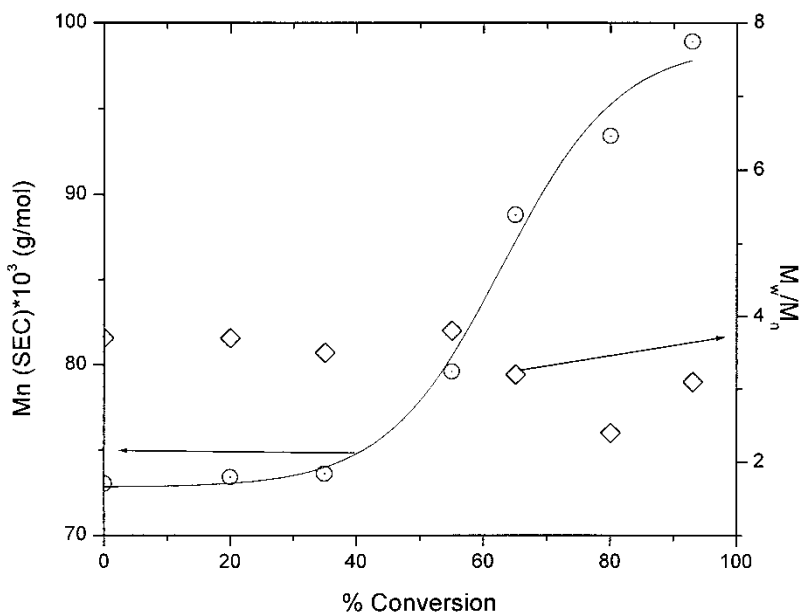


Figure 1. A plot of conversion vs. molecular weight and PDI for P(S-co-DS).

Table 1
Preparation of P(S-co-DS), P(S-co-BA) and P(S-co-TBA)

Thiobarbiturate polystyrene [P(S-co-TBA)] from P(S-co-DS)			Barbiturate polystyrene [P(S-co-BA)] from P(S-co-DS)		
% DPS	Ex. condition	% TBAPS	% DPS	Ex. condition	% BAPS
15	1 : 1 ratio of	15	15	1 : 1 ratio of	15
25	thiourea :	25	25	urea : sodium	25
40	sodium	40	40	methoxide,	40
60	methoxide,	60	60	12 hours	60
75	12 hours	75	75		75
92		92	92		92

Properties of Polystyrene with Various Compositions of the Hydroxybarbiturate and Hydroxythiobarbiturate P(S-co-BA) and P(S-co-TBA) Moieties

The fluorescence spectrum of PS with diethyl oxomalonate, hydroxy barbiturate and hydroxy thiobarbiturate pendant groups were recorded using an excitation wavelength of 300 nm. The fluorescence spectra for the sample corresponding to Table 1, entry 6 are shown in Fig. 2 and the data is summarized in Table 2. The emission maximum (E_m) of P(S-co-DS) (1 mg of polymer in 1 mL of THF) is 366 nm and that of P(S-co-BA) and P(S-co-TBA) (1 mg of polymer in 1 mL of water) are 403 nm and 385 nm, respectively. Compared to DPS, P(S-co-BA) is more conjugated and cyclic. Therefore, there is a red shift in the E_m and there is an increase in the fluorescence intensity as

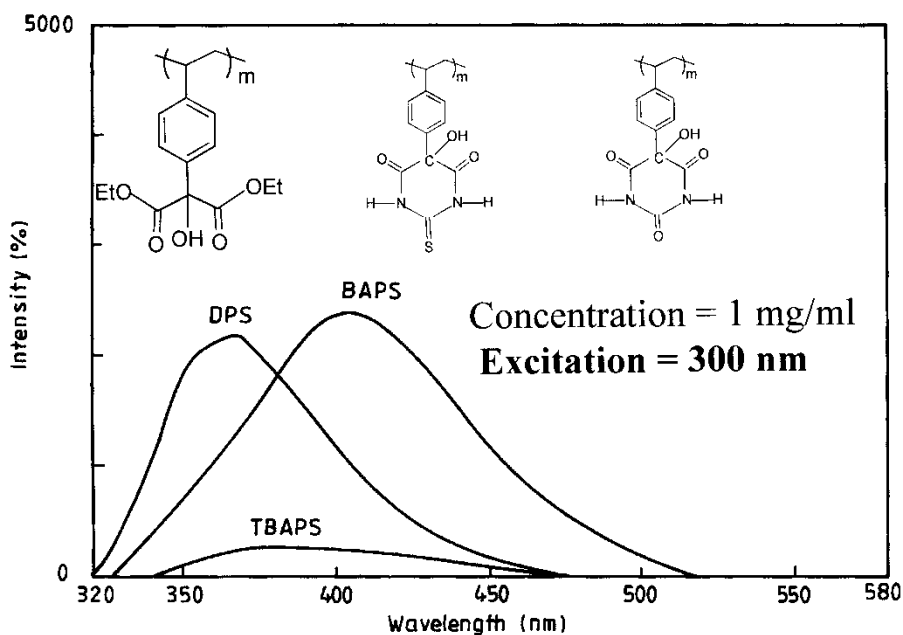


Figure 2. Fluorescence spectra of DPS, P(S-co-BA), and P(S-co-TBA).

Table 2
Intensity at emission maximum for DPS, P(S-co-BA) and P(S-co-TBA)
(92 mol% DS, BA and TBA moieties)

	P(S-co-DS)	P(S-co-BA)	P(S-co-TBA)
E_m	366	403	385
Intensity	2,208	2,402	272

well. In the case of P(S-co-TBA), although there is a slight red shift in the E_m , the fluorescence intensity decreases. This is probably due to the quenching of the excited state by the sulphur atom present in the hydroxy thiobarbiturate ring. A simple explanation for the trend in the red shift observed in the case of P(S-co-BA) and P(S-co-TBA) can be attributed to the change in solvent (THF for P(S-co-DS) and water for P(S-co-BA) and P(S-co-TBA)) as solvent polarity can influence the excited state from which emission occurs to the ground state. A more involved and meaningful explanation for the observed red shift can be attributed to the formation of twisted intramolecular charge transfer complex in the highly polar medium, and can be usually characterized by enhanced or reversed charged transfer associated with rotation around the phenyl-hydroxy thiobarbiturate ring. It is known that charge separation is favored in twisted conformations, where the two moieties involved, the donor and the acceptor, are orbitally decoupled.^[13]

The fluorescence emission in all cases is found to be concentration dependent for a particular mole fraction of the pendant moiety and this is estimated as well. The variation in the fluorescence emission for the polymers with varying mole fraction of oxomalonate (P(S-co-DS)) and barbiturate (P(S-co-BA)) moieties is depicted in Fig. 3. The fluorescence intensity of P(S-co-DS) (1 mg/ml in THF) increases with increasing mole fraction of the oxomalonate unit (Fig. 3a) as expected. A similar trend is also observed in the case of P(S-co-BA) (1 mg/ml in water) also, as shown in Fig. 3b. Interestingly, the fluorescence emission of P(S-co-BA) is more like P(S-co-DS) (366 nm) in the case of low mole fraction of P(S-co-BA) and as the mole fraction of barbiturate moiety increases, it moves towards the characteristic emission of fully converted P(S-co-BA) (403 nm) suggesting that the observed fluorescence behavior is due to the barbiturate moiety.

The introduction of pendant moieties, which in the small molecular form are water-soluble, in a predominantly hydrophobic polystyrene backbone suggested that these molecules might aggregate in solution. Polystyrene with a pendant group mole fraction of 0.2 [P(S-co-BA), P(S-co-TBA) as well as the copolymers] were soluble only in water (Experimental section) and even dilute solutions of concentration above 0.1 mg/ml were mildly translucent. To assess the possibility of aggregation in solution, surface tension measurement studies as a function of concentration of the polymer in solution were carried out. Surface tension measurement was performed using Gouy's surface tensiometer (standardized using distilled water and other liquids of known surface tension). A standard density of 1 mg/mL was used for all the solutions. The surface tension of P(S-co-BA) and P(S-co-TBA) decreased with increasing solution concentration as expected due to the presence of surface-active groups. After a particular concentration, surface tension remained constant as shown in Fig. 4, clearly confirming the formation of micelles via aggregation. Investigation of the dilute solutions of P(S-co-BA) and P(S-co-TBA) under an optical microscope (bright and fluorescence field) revealed the formation of fibrillar structure as shown in Fig. 5.

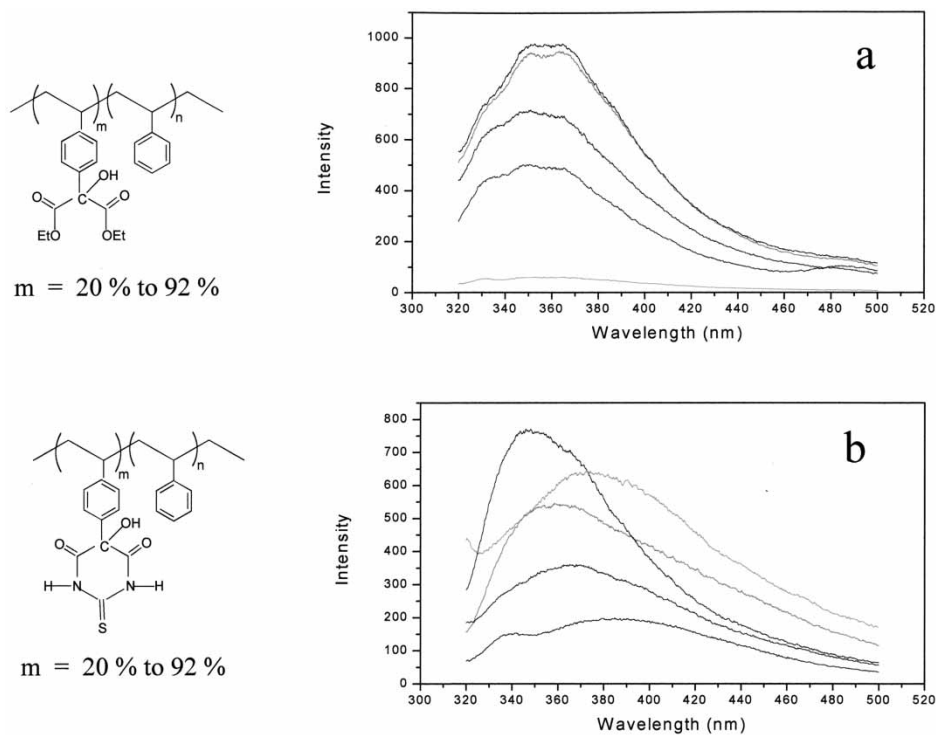


Figure 3. Fluorescence emission for the polymers with varying mole fraction of a) oxomalonnate (DPS) and b) barbiturate moieties.

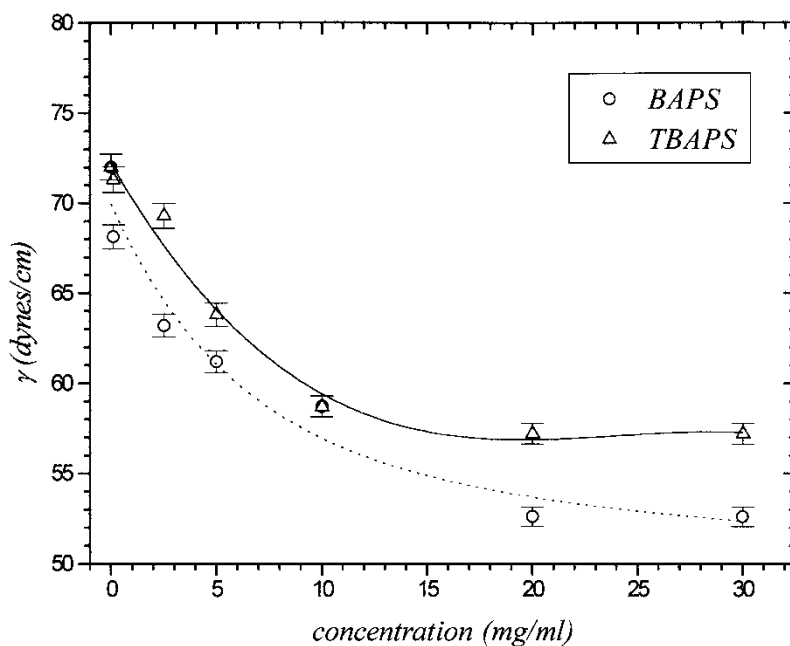


Figure 4. Surface tension measurement studies of P(S-co-BA), and P(S-co-TBA).

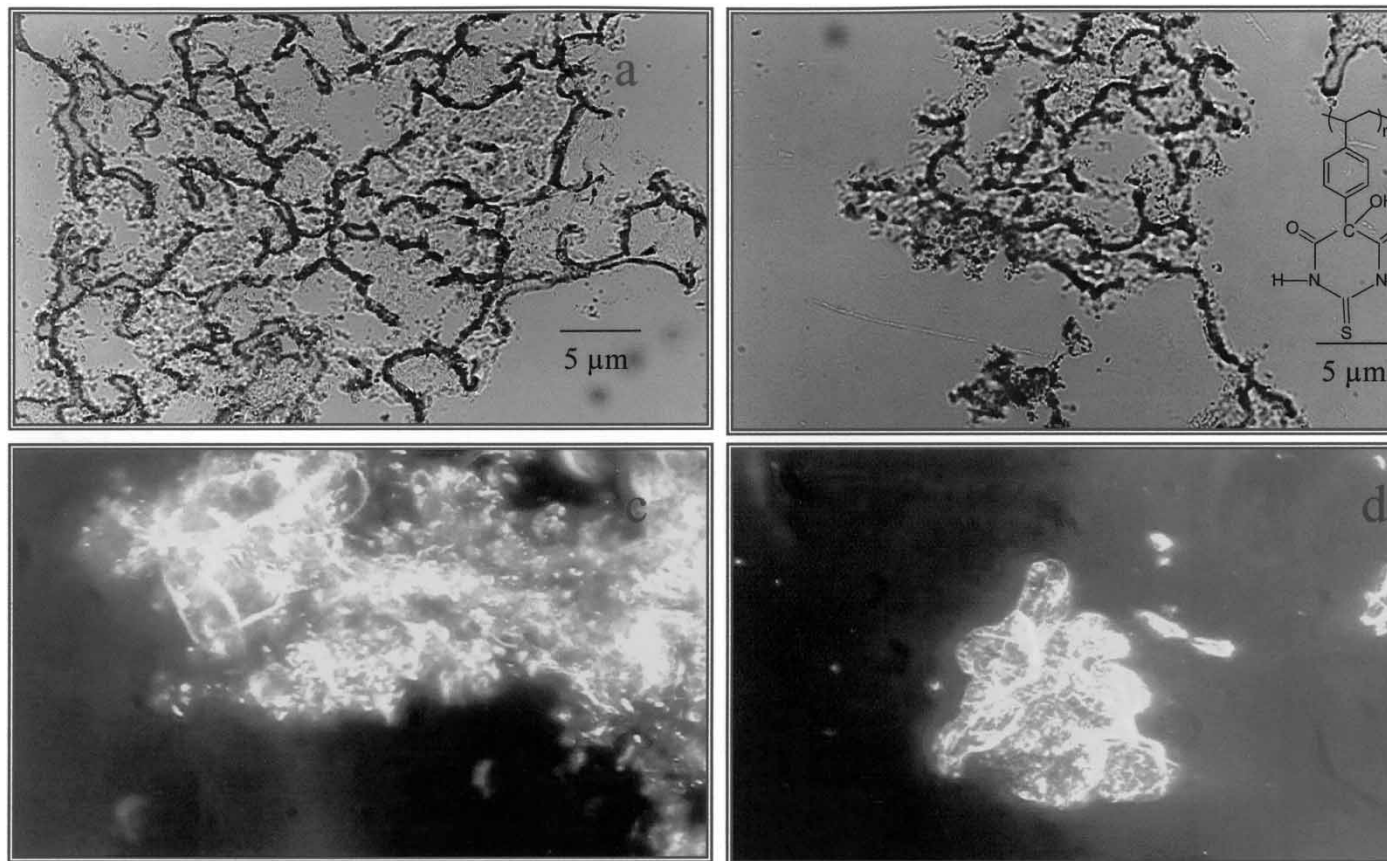


Figure 5. Fluorescence and bright field pictures of an aqueous solution (1 mg/mL) of P(S-co-BA) and P(S-co-TBA).

The addition of sodium chloride to the aqueous solution of the polymers resulted in the formation of a thick white precipitate. The addition of methanol in drops to an aqueous solution of P(S-co-TBA) or P(S-co-BA) (10 mg/ml) resulted in the formation of a thick white precipitate as shown in Fig. 6. The precipitate formation is also observed upon the addition of aqueous solutions of certain metal ions. On heating an aqueous solution of the polymer, a small portion was observed to precipitate at around 90°C, which redissolved on cooling. The above observations along with the molecular association observed in the solution state (as seen via microscopy) can be attributed to extensive hydrogen bonding which could result in the formation of liquid crystalline phase.

The barbiturate/thiobarbiturate moieties are known to bind to metal ions^[15] (as shown in Sch. 1) and it was observed that both the polymers bind to a variety of metal ions such as Cu^{+2} , Fe^{+2} , Ni^{+2} , Mn^{+2} , Zn^{+2} , Hg^{+2} , and Co^{+3} . The degree (ppm) of metal chelation/uptake was established by atomic absorption spectroscopy and/or UV absorption spectroscopy. The results from this study are summarized in Table 3. One specific example pertaining to Cu^{+2} uptake is discussed here. The extent of Cu^{+2} ion coordination was investigated via atomic absorption spectroscopy (AAS). Because AAS is a more widely used and accepted analytical tool for the precise determination of trace quantities of metal ions, the capacity of TBAPS and BAPS to remove metal ions from an aqueous solution was assessed by AAS. The chelating ability of the polymer with various mole fractions of BA and TBA (0.2 to 0.94%) unit were studied. The extent of metal ion coordination was investigated via atomic absorption spectroscopy (Figs. 7 and 8) as well as by UV spectroscopy (Fig. 9). A plot of the mol% of TBA pendant functionality versus the amount of copper present in the filtrate measured using AAS is shown in Fig. 7. It is clear that the amount of copper ion uptake is higher in the case of the polymer with a higher mole % of the TBA pendant group for the same initial mass of polymer taken for analysis. This is consistent with the spectrophotometric findings (Fig. 9). The metal chelating ability was observed to vary with the amount of

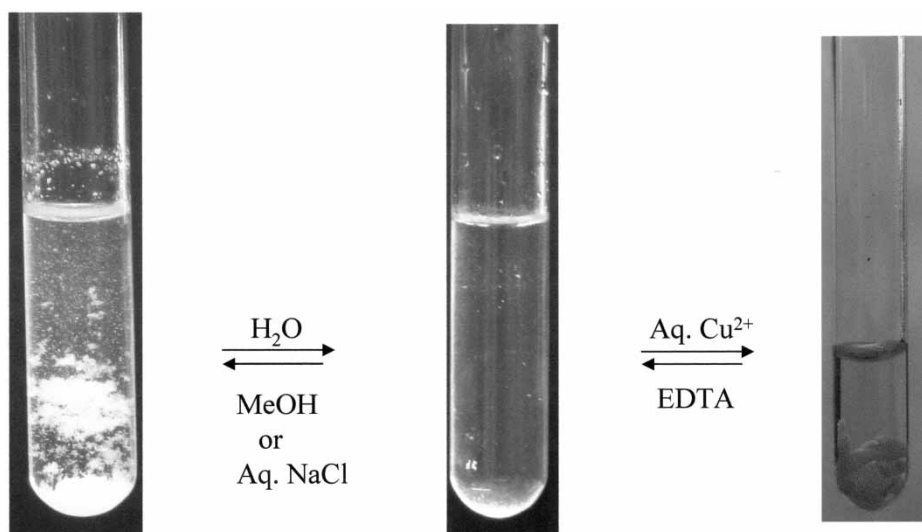
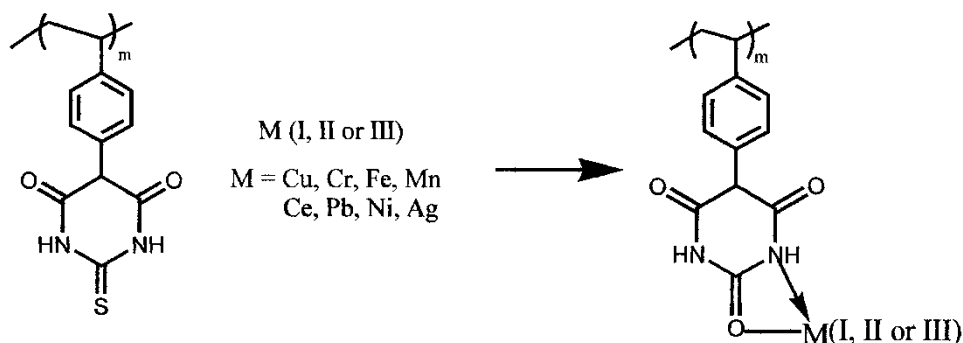


Figure 6. Reversible precipitation and dissolution upon the addition of specific chemical reagents such as methanol or an aqueous solution of NaCl or an aqueous solution of CuSO_4 .



Scheme 1. Mechanism for the metal chelation of TBAPS with various metal ions.

polymer used (mg), for a polymer of given mole % functional groups, as revealed in Fig. 8. The polymers developed in this study are water-soluble and exhibit metal ion binding capacities in the range of 3 to 4 milliequivalents/gram of resin. This compares well with typical commercial resins (porous, insoluble, crosslinked), which exhibit metal ion binding capacities in the range of 3 to 5 milliequivalents/gram of resin. The most important advantage of the polymers presented in this paper is that rapid ease with which metal ions are extracted from solution (it is instantaneous) in view of their water solubility. The removal of the metal from the metal-bound polymers was performed with 5 M HCl and the metal free polymers (this was followed by UV; data not shown) upon neutralization, was found to be as effective as the original polymers (up to 5 recycling studies were conducted).

To assess the thermal stability of P(S-co-BA) and P(S-co-TBA) as a function of the mole fraction of the pendant groups. The TGA was performed under nitrogen atmosphere. The initial decomposition temperature of P(S-co-BA) and P(S-co-TBA) (70°C) is considerably lower and this is due to the dehydration/decomposition of the three-hydroxyl groups present as a part of the barbiturate moiety, much before any other thermal transformations. The mass loss of 20–21% in the temperature range of ambient to 200°C is also consistent with the loss of three hydroxyl groups for P(S-co-BA) and P(S-co-TBA) with 92 mol% functional groups. The interesting aspect of this study is the large

Table 3
Percent uptake of various metal ions in the case of P(S-co-TBA) with
92 mol% of TBA functional groups

Divalent metal ions	Metal ion present in the analyte (ppm)	Metal present in the filtrate (ppm)	% In terms of uptake
Fe	16.76	3.89	77
Co	17.62	4.19	76
Ni	17.62	5.48	69
Mn	16.50	4.90	70
Zn	19.61	8.60	56
Cu	19.05	2.23	88

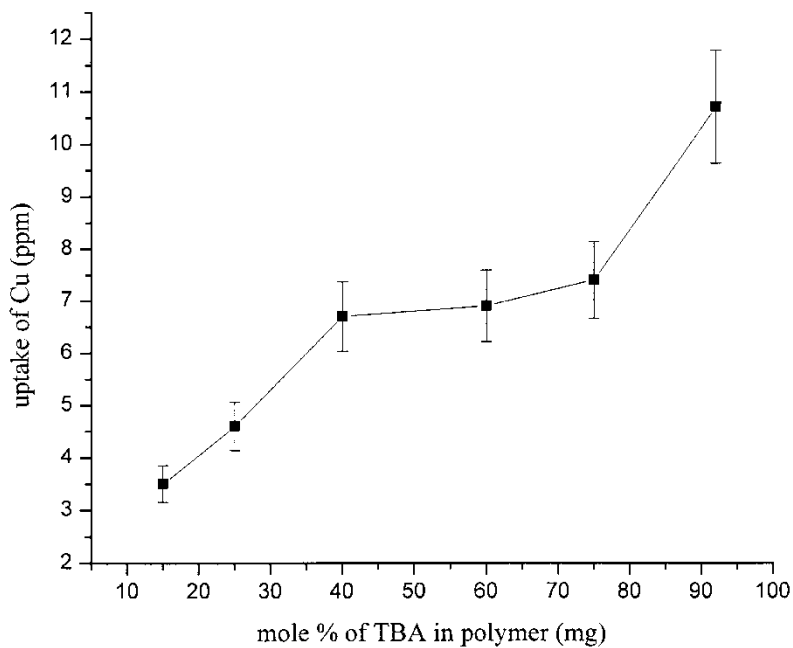


Figure 7. Extent of Cu^{+2} uptake vs. mol% of TBA functionality (AAS data).

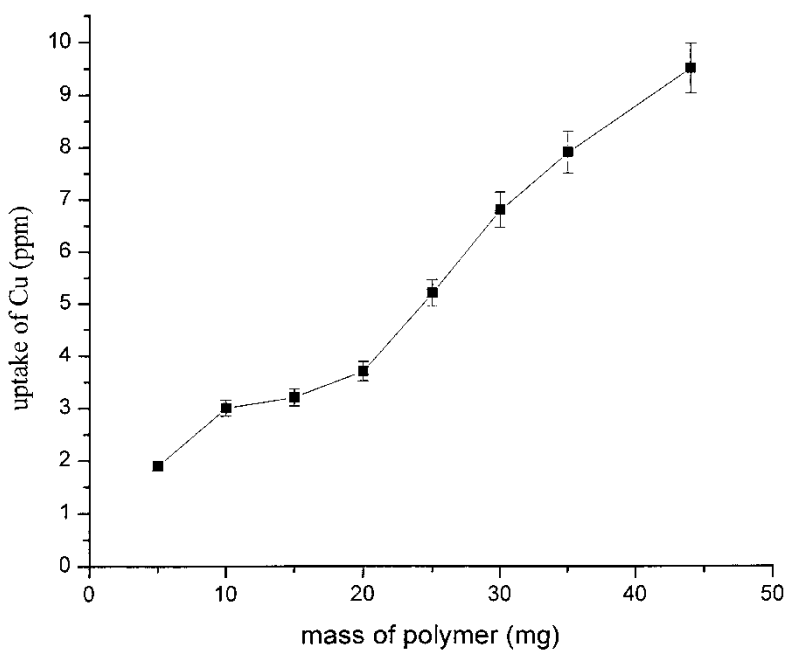


Figure 8. Extent of Cu^{+2} uptake versus mass of P(S-co-TBA) (92 mol% of TBA functionality; AAS data).

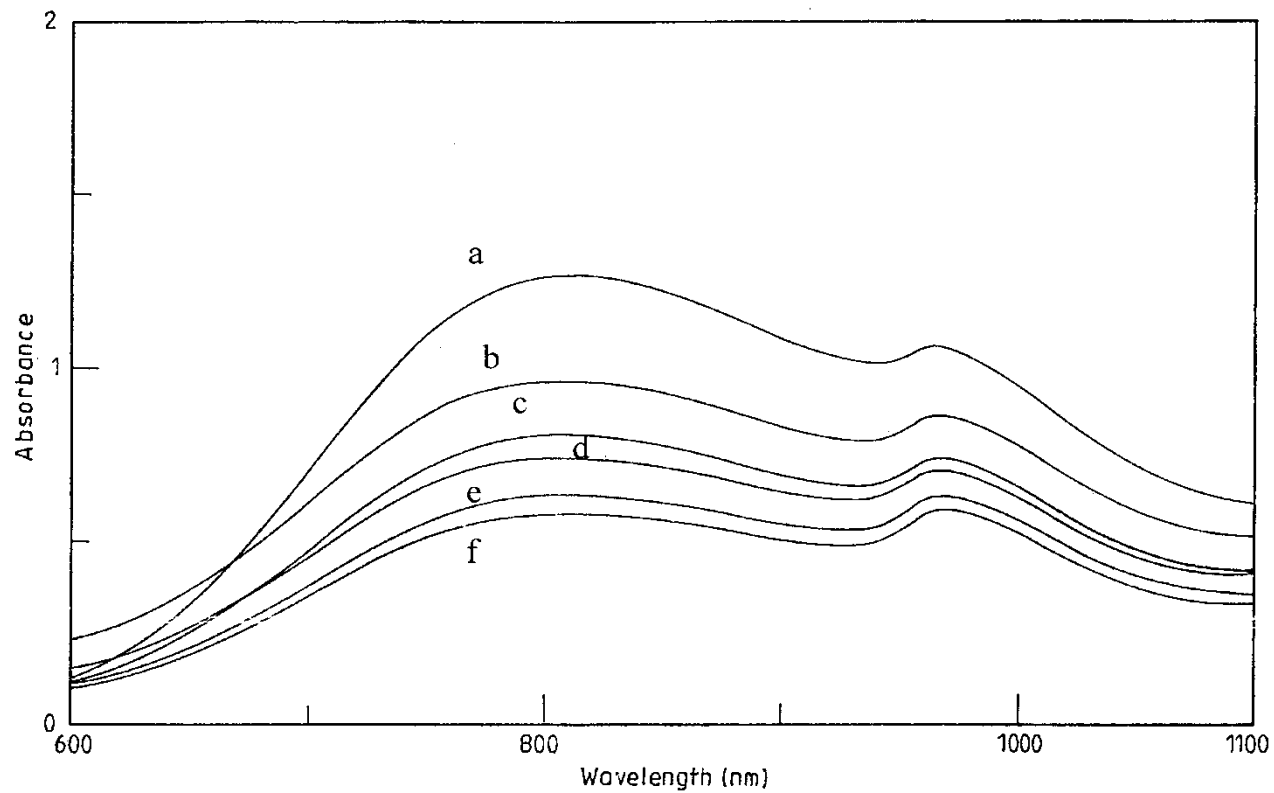


Figure 9. Absorption spectrum of CuSO₄·5 H₂O (0.1 M; a) upon the addition of P(S-co-TBA) (25 mg each) of 25 (b), 40 (c), 75 (d), and 92 (e) mol% of TBA functional groups.

quantity of residue (35 to 70 wt%) left at the end of the study, which increased with increasing mol% of BA and TBA pendant groups (data not shown here).

Conclusions

The introduction and selective control of pendant groups on the backbone structure of a purely amorphous polymer, such as atactic polystyrene, results in enhanced fluorescence for the hydroxy barbiturate pendant moiety while it is reduced for the hydroxy thiobarbiturate moiety. The extent of fluorescence is shown to be linearly dependent on the mole fraction of the pendant groups. Further surface activity in aqueous solution is shown to be dependent on the concentration of the functional groups as well. Hydroxy barbiturate and hydroxy thiobarbiturate functionalized polystyrenes are observed to form an organized assembly in a dilute aqueous solution, which is disrupted by the addition of specific chemical reagents such as methanol, aqueous NaCl and aqueous CuSO₄. This organization might be due to hydrogen bonding. The polymers synthesized are observed to chelate to a wide variety of metal ions, the % uptake of which is observed to increase with increasing mol% of the pendant functional groups.

Acknowledgment

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