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ScienceDirect
Polymer 47 (2006) 8088–8094
polymer
www.elsevier.com/locate/polymer

Induction of chirality into a fully sulfonated poly(methoxyaniline) via acid–base interactions with chiral amines

Ekaterina V. Strounina, Leon A.P. Kane-Maguire*, Gordon G. Wallace*

ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

Received 24 May 2006; received in revised form 31 August 2006; accepted 1 September 2006

Abstract

A wide range of chiral amines and amino alcohols associate with poly(2-methoxyaniline-5-sulfonic acid) (PMAS) in aqueous solution, from which optically active PMAS·(amine) films can be cast. The chiral induction is believed to be initiated by acid–base interactions with "free" sulfonic acid groups on the PMAS chains. Chiral amine:PMAS dimer molar ratios as low as 1:4 give PMAS·(amine) films with similar optical activity to those cast from 1:1 molar mixtures, indicating that only one in four of the "free" sulfonate groups on the PMAS chains need to be electrostatically bound by chiral ammonium ions to achieve optimal chiral induction. Circular dichroism studies show that the enantiomeric amines (*R*)-(+)- and (S)-(−)-1-phenylethylamine induce the opposite helical hands for the supermolecular assemblies of PMAS chains. However, there is no clear correlation between the sign of the CD signals for the PMAS·(amine) films and the configuration of structurally diverse amines.

Keywords: Polymer chemistry; Polymer synthesis; Polymer physical chemistry

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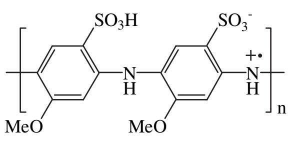
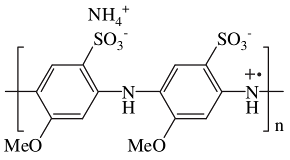
1. Introduction

Sulfonated polyanilines have attracted considerable recent attention due to the water solubility of their self-doped emeraldine salt forms. The first fully sulfonated polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS), was initially prepared [1] via chemical oxidation of the 2-methoxyaniline-5-sulfonic acid (MAS) monomer, and subsequently [2] by electrochemical polymerisation. It has significant advantages compared to previously prepared 50–75% sulfonated polyanilines (SPANs) due to its markedly higher solubility in water (greater than 10% w/v). In the PMAS dimer repeat unit **1a**, one sulfonic acid substituent is involved in self-doping an adjacent radical cation nitrogen site, while the other acid functional group is "free". Due to the presence of ammonia in the polymerisation mixture (to assist solubilisation of the MAS monomer), the PMAS polymer is typically obtained as a mixture of the acid PMAS(H^+) **1a** and ammonium PMAS(NH_4^+) **1b** forms.



1a



1b

There is much current interest in the preparation of chiral conducting polymers because of their demonstrated potential as novel chiral materials for the identification/separation of enantiomeric chemicals [3,4], as chiral electrodes in electrochemical asymmetric synthesis [5], and as chemical and biological sensors [6]. Optically active polyaniline emeraldine salts (PAni·HA) have been prepared via the incorporation of

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* Corresponding authors. Tel.: +61 2 4221 3127; fax: +61 2 4221 3114.
E-mail address: gordon_wallace@uow.edu.au (G.G. Wallace).

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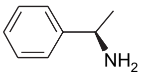
doi:10.1016/j.polymer.2006.09.024

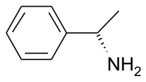
chiral dopant anions (A^-) either (i) during electrochemical polymerisation of aqueous aniline in the presence of a chiral dopant acid HA [7], or (ii) by acid doping of emeraldine base with the chiral acid in an organic solvent such as 1-methyl-2-pyrrolidinone (NMP) [8,9].

Optically active PMAS materials have been prepared via the electrochemical polymerisation of MAS monomer in the presence of the chiral amines (*R*)-(+)- or (*S*)-(−)-1-phenylethylamine (PhEA), resulting in the deposition of optically active PMAS·(+)-PhEA and PMAS·(−)-PhEA films [10]. Their observed visible region optical activity was suggested to arise from the adoption of a preferred one-handed helical structure by the PMAS polymer chains, due to acid–base interactions between the chiral amines and “free” sulfonic acid groups on the polymer.

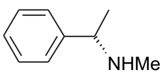
We report here an alternative and potentially widely applicable route to optically active PMAS via treating pre-formed aqueous PMAS(NH_4^+) with chiral amino species and spin casting to give optically active PMAS·(amine) films. A range of chiral amines are examined, namely (*R*)-(+)- and (*S*)-(−)-1-PhEA, (*S*)-(−)-*N*,α-dimethylbenzylamine (DMBA), (*S*)-(+)-1-cyclohexylethylamine (CHEA), (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine (BNDA), as well as the amino alcohols (*R*)-(−)-2-amino-1-propanol (AP) and (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (ADPE). Each of these compounds bears a stereogenic carbon centre adjacent to the amine functional group, except for (S)-(−)-BNDA which possesses axial chirality associated with the carbon–carbon bond linking the two naphthyl moieties.



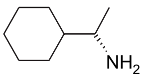
(*R*)-(+)-PhEA



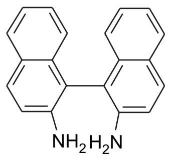
(*S*)-(-)-PhEA



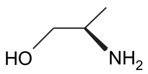
(*S*)-(-)-DMBA



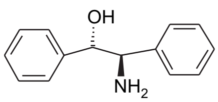
(*S*)-(+)-CHEA



(*S*)-(-)-BNDA



(*R*)-(-)-AP



(1*S*,2*R*)-(+)-ADPE

The chiroptical properties of the novel PMAS·(amine) polymers are described both in aqueous solution and as cast films. Circular dichroism studies suggest that the induced optical activity is associated with the formation of chiral aggregates of PMAS chains rather than one-handed helicity of individual polymer chains.

2. Experimental

2.1. Materials

PMAS was obtained from Mitsubishi Rayon Ltd. (Japan) and used as received. The chiral amines (*R*)-(+)- and (*S*)-(−)-1-PhEA, (*S*)-(−)-DMBA, (*S*)-(+)-CHEA, (*S*)-(−)-BNDA, and the amino alcohols (1*S*,2*R*)-(+)-ADPE and (*R*)-(−)-AP were obtained from Aldrich Chemical Co. and used without further purification. All aqueous solutions were prepared using Millipore water. Glass slides were cleaned with detergent, rinsed with isopropanol, dried and then exposed to a UVO-cleaner (Jelight Co. Inc.) for 5 min.

2.2. Preparation of PMAS·(amine) films

As detailed below, PMAS·(amine) films were spun-cast onto glass slides from aqueous mixtures of 3–5% (w/v) PMAS(NH_4^+) with the various chiral amines and amino alcohols, using a Photo-Resist Spinner (Headway Research Inc) and a spinning speed of 2000 rpm. In the case of chiral amines with poor water solubility, the amine was dissolved in an organic solvent prior to addition to aqueous PMAS.

1. (+)-PhEA, (−)-PhEA, (−)-AP and (+)-CHEA have good water solubility. These were mixed with 5 ml of aqueous 5% (w/v) PMAS(NH_4^+) in an amine:PMAS dimer molar ratio of 1:1. After 2 h the PMAS·(amine) polymer films were coated onto glass slides via spin casting.
2. (−)-DMBA was dissolved in 0.5 ml of acetone and (+)-ADPE was dissolved in 1 ml acetone, and then each separately mixed with 5 ml of aqueous 5% (w/v) PMAS in an amine:PMAS dimer ratio of 1:1. Samples were spun-cast onto glass slides after 2 h.
3. (−)-BNDA (10 mg) was dissolved in 1.5 ml of acetonitrile and mixed with 1.5 ml of aqueous 3% PMAS, giving an amine group:PMAS dimer ratio of 0.70. The mixture was spun-cast after 2 h.
4. To study the influence of the chiral amine concentration on chirality induction by (+)-PhEA and (−)-DMBA, the amine:PMAS dimer ratio was decreased from 1:1 to 1:2, 1:4 and 1:8. The rest of the procedure was carried out as described above.

2.3. UV–visible-near infrared and CD spectroscopic studies

The glass mounted PMAS·(amine) polymer films were kept in a desiccator over silica gel. Their UV–visible-near infrared and circular dichroism (CD) spectra were recorded at room temperature using a Cary 500 spectrophotometer and a Jobin Yvon Dichrograph 6, respectively.

3. Results and discussion

Aqueous solutions of the PMAS(NH_4^+) starting material employed in this study were khaki/brown in colour. Their

UV–visible spectra differed from that of parent polyaniline emeraldine salts (PAni·HA) or SPANs, exhibiting overlapping bands between 320 and 390 nm attributable to π–π* transitions [11,12] and a characteristic sharp peak at ca. 473 nm. This latter peak has been assigned as a low wavelength polaron band, red-shifted from that observed in other emeraldine salts [11,12]. Unlike "compact coil" polyanilines [13], aqueous PMAS did not exhibit a localised polaron band in the 700–900 nm region, but instead showed a broad near-infrared absorption band at wavelengths greater than 1000 nm. This indicates a delocalised polaron band typical of emeraldine salts in an "extended coil" conformation [13,14].

3.1. Interaction of aqueous PMAS(NH_4^+) with (+)- and (−)-PhEA

An aqueous mixture of PMAS(NH_4^+) with (+)-PhEA (amine:PMAS dimer ratio of 1:1) exhibited a UV–visible-near infrared spectrum (Fig. 1a) very similar to that of PMAS(NH_4^+) itself, showing a characteristic intense band (slightly red-shifted) at 483 nm. Confirmation of the interaction between the chiral PhEA and the PMAS polymer chains (presumably involving replacement of the NH_4^+ ions in structure **1b** by protonated (+)-PhEA) was obtained from the corresponding CD spectrum which showed the generation of visible region optical activity (Fig. 1b). The CD spectrum was similar (but of lower intensity) to that found previously [10] for electrochemically generated PMAS·(+)-PhEA films. A bisignate CD signal was observed centred at ca. 500 nm, associated with the PMAS absorption band at 483 nm, together with weaker CD signals at lower wavelengths associated with the broad absorptions of PMAS in the 330–380 nm region.

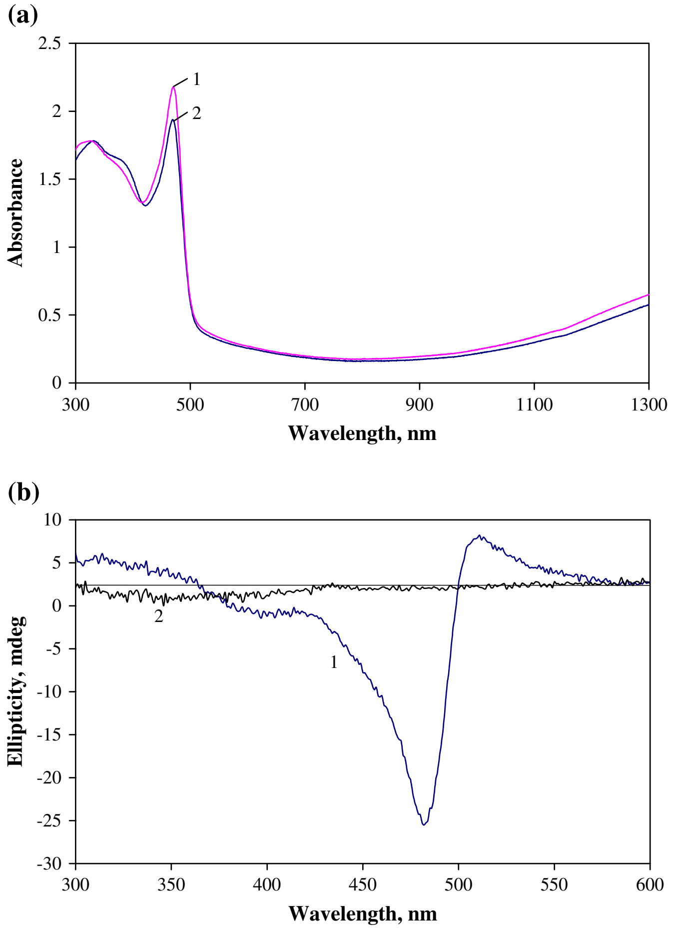


Fig. 1. (a) UV–visible-near infrared spectra of a 1:1 aqueous PMAS·(+)-PhEA mixture: (1) unfiltered and (2) filtered. (b) CD spectra of the 1:1 aqueous PMAS·(+)-PhEA mixture from (a) recorded 1 h after mixing: (1) unfiltered and (2) filtered.

Significantly, unlike the absorption spectrum which was little affected by filtration (Fig. 1a), filtering the PMAS/(+)-PhEA mixture through a 0.45 μm filter caused the loss of all CD signals (Fig. 1b). This loss of optical activity indicates that the optical activity observed for aqueous PMAS/(+)-PhEA mixtures is associated with microparticles of aggregated PMAS·(+)-PhEA chains rather than molecular chirality induced in individual polymer chains. The supermolecular assemblies of PMAS chains are believed to adopt a predominantly one-handed helical arrangement under the influence of the chiral amine. A similar conclusion has been reached for chiral polythiophenes in an elegant series of studies by Meijer et al. [15] in a range of organic solvents. Data obtained by Okamoto et al. [16] for optically active polyacetylenes bearing chiral oxazoline residues agree with this hypothesis.

3.2. Chiroptical properties of PMAS·(+)-PhEA films

The UV–visible region of the spectra of spun-cast PMAS·(+)-PhEA and PMAS·(−)-PhEA films (Fig. 2a) was similar to that of their precursor aqueous solutions prior to casting (Fig. 1a), exhibited π–π* bands between 300 and 400 nm and a sharp polaron band at ca. 480 nm. The near-infrared region could also be examined for the films, revealing a strong broad band centred at ca. 2000 nm (Fig. 2a). A very similar near-infrared band has been reported [10] for electrochemically generated PMAS·PhEA films, and is considered characteristic [13,14] of a polyaniline emeraldine salt in an "extended coil" conformation.

The spun-cast PMAS·PhEA films were strongly optically active, as revealed by their CD spectra (Fig. 2b). The observed CD bands do not arise from the chiral (+)-PhEA and (−)-PhEA ammonium ions present in the films, as these cations only absorb in the UV region. The visible region CD spectra of the PMAS·PhEA films may therefore be attributed to the polymeric PMAS moiety.

Like the related electrochemically generated films [10], the spun-cast PMAS·(+)-PhEA and PMAS·(−)-PhEA films in Fig. 2b exhibited bisignate exciton-coupled CD bands at ca. 310 and 405 nm associated with the absorption bands of PMAS at 330–380 nm as well as further CD bands at ca. 480 and 520 nm associated with the PMAS 480 nm polaron absorption band. However, a significant difference from the previous electrochemically deposited films is the very weak intensity of the high wavelength component of the bisignate CD signals centred at 500 nm (Fig. 2b). The failure to observe significant Davydov splitting of this CD band indicates only

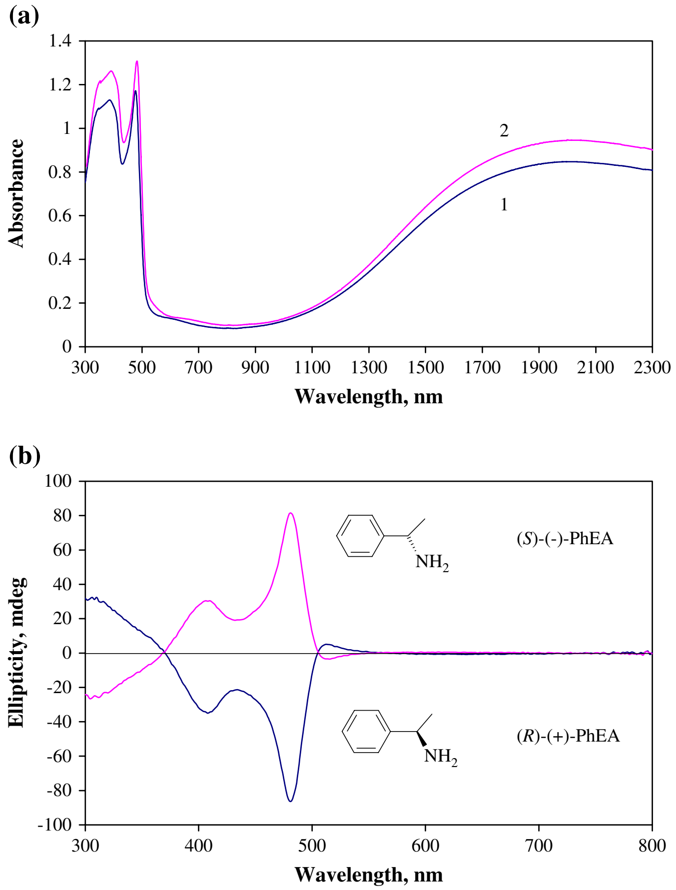


Fig. 2. (a) UV–visible-near infrared spectra of PMAS·PhEA films spun-cast from 1:1 aqueous 5% (w/v) (1) PMAS/(+)-PhEA and (2) PMAS/(−)-PhEA mixtures. (b) CD spectra of the spun-cast 1:1 PMAS·(+)-PhEA and PMAS·(−)-PhEA films from (a).

minor exciton coupling between the responsible chromophores [18,19], either on the same or adjacent PMAS chains. One may therefore conclude that the polaron chromophores in PMAS·PhEA emeraldine salts are more separated in spun-cast films. It is uncertain at present why spin-casting should cause this effect, although MacDiarmid et al. [20] have suggested that the shear forces in spin-casting can lead to disentanglement of polyaniline chains and a more "extended coil" conformation.

The induction of optical activity in PMAS is believed to arise from electrostatic bonding of (+)-PhEA or (−)-PhEA ammonium ions to ionised sulfonate groups along the PMAS backbone, inducing the polymer to preferentially adopt a one-handed helical structure. Okamoto et al. [17] have reported similar induction of optical activity in poly{(4-carboxyphenyl)-acetylene} via acid–base interaction with chiral amines. The helical chirality in the PMAS·PhEA emeraldine salts could be associated with the presence of either one-handed individual helical PMAS chains or a supermolecular helical assembly of aggregated polymer chains (as proposed for chiral polythiophenes [15]). The latter model is favoured on the basis of the effect of filtering on the CD spectra of aqueous PMAS·(+)-PhEA mixtures (see Section 3.1).

The spun-cast PMAS·(+)-PhEA and PMAS·(−)-PhEA films exhibited the expected mirror image CD spectra (Fig. 2b), indicating that enantiomeric (+)- and (−)-PhEA ammonium cations induce opposite helical senses in the aggregated PMAS chains.

3.3. Chiral induction by other chiral amines

3.3.1. Chiral amines with stereogenic carbon centres

Two other chiral amines bearing stereogenic carbon centres adjacent to the amino group were similarly investigated as potential chiral inducing agents for the preparation of optically active PMAS·(amine) films. (*S*)-(+)-1-Cyclohexylethylamine (CHEA) differs from the PhEA studied above by the replacement of its phenyl ring by a less rigid cyclohexyl ring. On the other hand, (*S*)-(−)-*N*,α-dimethylbenzylamine (DMBA) is the *N*-methyl derivative of (*S*)-(−)-PhEA.

UV–visible-near infrared spectra of spun-cast films of PMAS with (S)-(+)-CHEA and (*S*)-(−)-DMBA are shown in Fig. 3. Both films displayed characteristic features of PMAS, having a sharp peak at ca. 465 nm and a broad, strong band in the near infrared region with λ_{max} at $\geq$2050 nm. Their corresponding CD spectra (Fig. 4a and b) showed similar features to the PMAS·(+)-PhEA film, including the virtual absence of bisignate character for the CD band associated with the 465 nm polaron absorption band. Instead, they showed strong negative CD bands at ca. 480 and 495 nm, respectively (with little or no evidence of a higher wavelength component of opposite sign). Interestingly, the negative sign of these 480 and 495 nm CD bands is the inverse of that observed in Fig. 2b for the PMAS·(−)-PhEA film, where the PhEA has the same *S*-configuration. This lack of correlation indicates that the sign of the CD bands for related chiral amines cannot be used to predict the configuration of the amine bound to the PMAS. The different signs of the CD bands must reflect different steric and electronic interactions by the amines during their stereoselective acid–base interactions with sulfonate groups on the PMAS chains.

The magnitude of the optical activity induced into PMAS by the various chiral amines in the spun-cast PMAS·(amine) films is summarised in Table 1 in terms of the calculated chiral

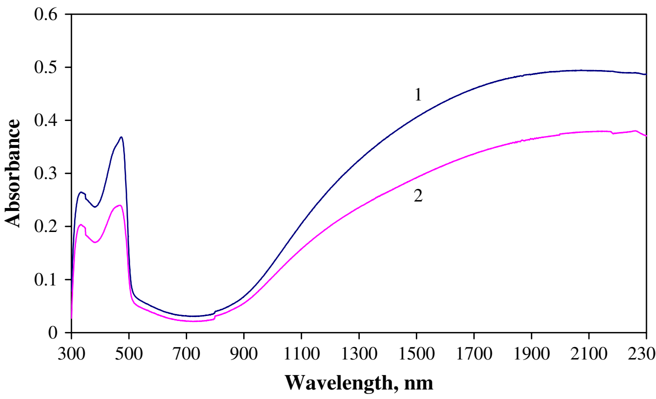


Fig. 3. UV–visible-near infrared spectra of PMAS·(amine) films spun-cast from 1:1 aqueous mixtures of PMAS with (1) (+)-CHEA, and (2) (−)-DMBA.

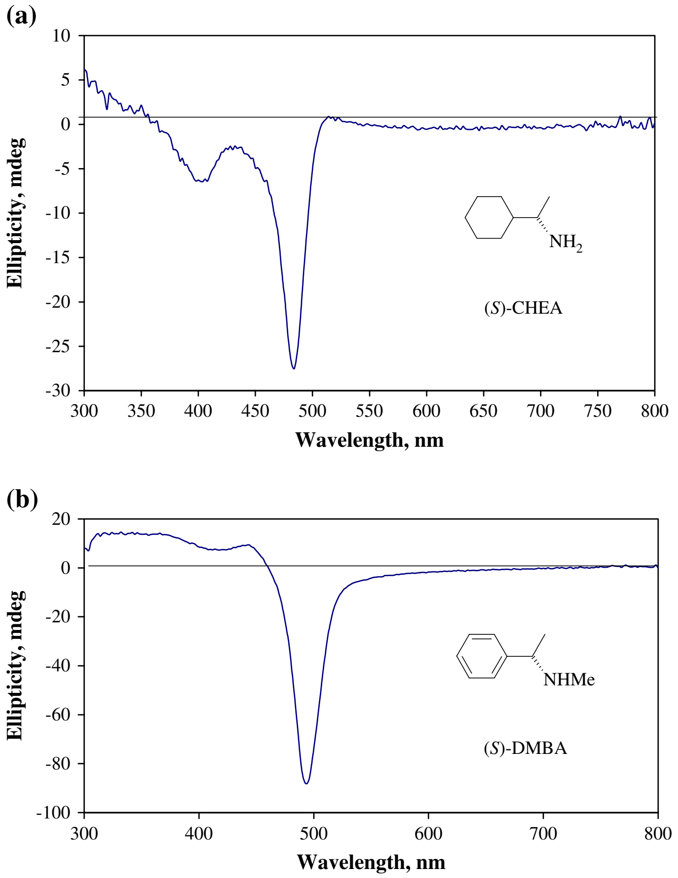


Fig. 4. CD spectrum of the spun-cast (a) 1:1 PMAS·(+)-CHEA and (b) 1:1 PMAS·(−)-DMBA films from Fig. 3.

anisotropy factors. PMAS·(+)-CHEA and PMAS·(+)-PhEA films have similar Δε/ε values (0.23 and 0.22%, respectively), indicating that the presence of a saturated cyclohexyl ring in the incorporated amine instead of a phenyl ring has little influence on the magnitude of chiral induction in the PMAS chains. The PMAS·(−)-DMBA film was the most optically active, with a Δε/ε value of 1.09% at 495 nm (Table 1). This marked increase in chiral induction caused by the *N*-methyl substituent in this secondary amine compared to (+)-PhEA has parallels in other studies of chiral discrimination.

3.3.2. BNDA — an amine with a chiral axis

The amine (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine (BNDA) differs from the other amines in this study in that its source of chirality is a chiral axis between the two naphthyl moieties rather than a stereogenic carbon centre. In addition, it possesses two amine centres which may give enhanced possibilities for acid–base interactions with SO_3H groups on PMAS chains. Nevertheless, chiral induction by this diamine is apparently hindered by its bulky nature. Although the UV–visible-near infrared spectrum of the spun-cast PMAS·(−)-BNDA film (Fig. 5a) was similar to that of the other spun-cast PMAS·(amine) films (and was not affected by the presence of acetonitrile in the casting mixture), its CD spectrum (Fig. 5b) revealed only weak optical activity (Δε/ε = 0.07% for its 485 nm CD band).

Table 1
Chiral anisotropy factors (Δε/ε) for chiral 1:1 PMAS·(amine) films

PMAS·(amine)	Δε/ε, %
PMAS·(−)-BNDA	0.07
PMAS·(+)-PhEA	0.22
PMAS·(−)-PhEA	0.21
PMAS·(+)-CHEA	0.23
PMAS·(−)-DMBA/acetone	1.09
PMAS·(−)-AP	0.13
PMAS·(+)-ADPE/acetone	0.57

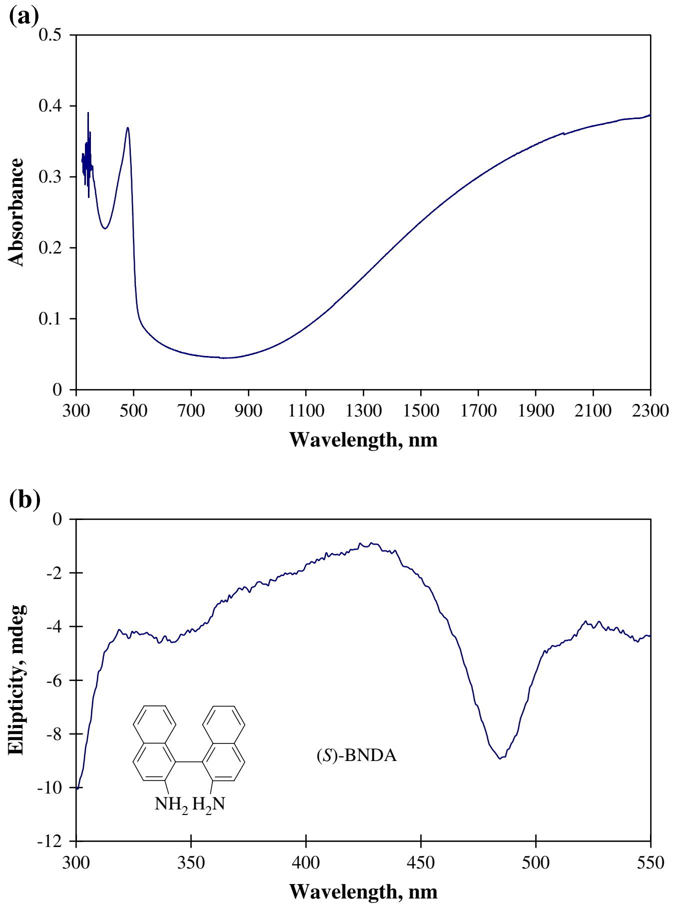


Fig. 5. (a) UV–visible-near infrared spectrum of a spun-cast 1:1 PMAS·(−)-BNDA film. (b) CD spectrum of the spun-cast 1:1 PMAS·(−)-BNDA film from (a).

3.3.3. Chiral amino alcohols

The ability of chiral amino alcohols to induce optical activity into PMAS was investigated with (*R*)-(−)-2-amino-1-propanol (AP) and (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (ADPE). The UV–visible-near infrared spectra of spun-cast 1:1 PMAS·(−)-AP and PMAS·(+)-ADPE films (Fig. 6) were similar to the spectra of the above PMAS·(amine) films, with characteristic peaks at ca. 470 nm. Their CD spectra (Fig. 7a and b) exhibited well-defined bands at 480 nm and broad weak bands in the 350–450 nm region. The absence again of bisignate CD signals indicated no exciton coupling between the responsible chromophores, either on adjacent or the same PMAS chains.

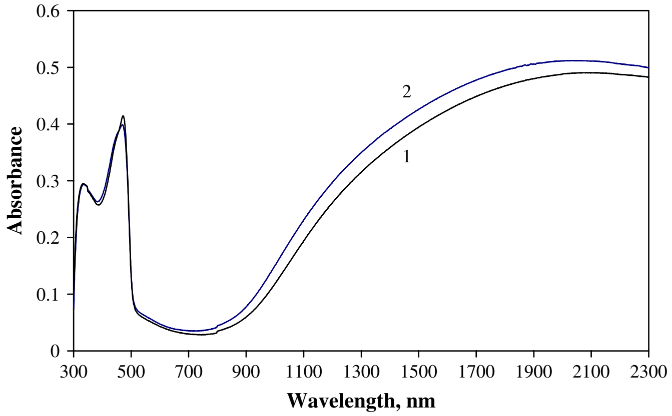


Fig. 6. UV–visible-near infrared spectra obtained for PMAS·(amino alcohol) films spun-cast from 1:1 mixtures of PMAS with (1) (−)-AP and (2) (+)-ADPE.

Table 2
Chiral anisotropy factors ($\Delta\varepsilon/\varepsilon$) obtained for PMAS·(amine) films of different amine:PMAS ratios

PMAS·(amine)	Amine:PMAS dimer ratio	$\Delta\varepsilon/\varepsilon$, %
PMAS·(+)-PhEA	1:1	0.21
	1:2	0.70
	1:4	0.57
PMAS·(−)-DMBA	1:1	0.39
	1:2	0.33
	1:4	0.31

Okamoto et al. [17] reported that chiral amino alcohols induced substantially stronger signals in the CD spectra of poly{(4-carboxyphenyl)acetylene} than did amines. They attributed this to additional H-bond formation between the hydroxy group of the amino alcohol and the carboxyl substituent of the polyacetylene. This trend was not confirmed in the present study with (−)-2-amino-1-propanol, which exhibited a lower $\Delta\varepsilon/\varepsilon$ value (0.13%) than found with (+)- or (−)-PhEA (see Table 1). However, the amino alcohol (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (ADPE) did show significantly enhanced chiral induction compared to all the amines studied (except the secondary amine (−)-DMBA), with the PMAS·(−)-ADPE film having a chiral anisotropy factor of 0.57%.

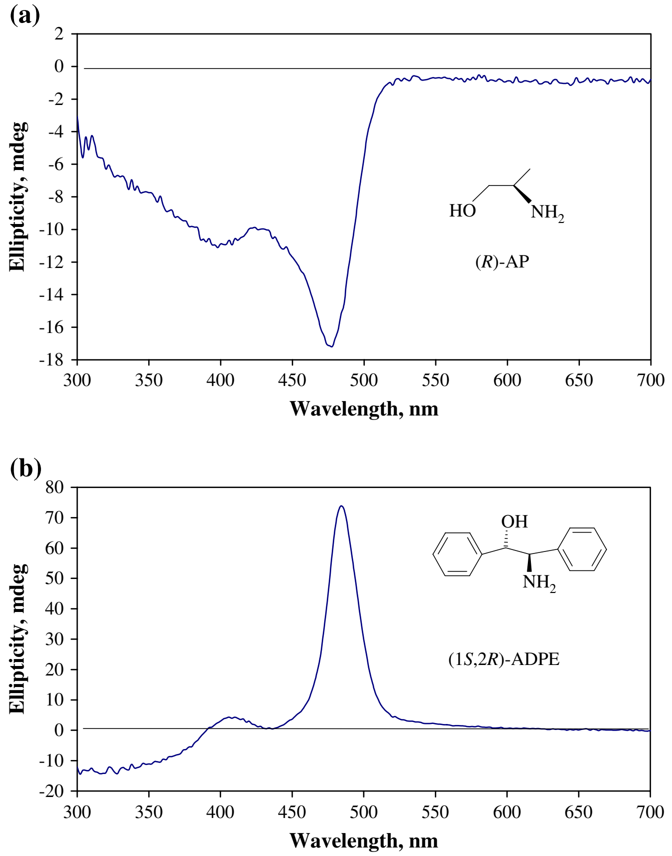


Fig. 7. CD spectrum of the spun-cast (a) 1:1 PMAS·(−)-AP and (b) 1:1 PMAS·(+)-ADPE films from Fig. 6.

Overall, there seems to be no obvious correlation between the configuration at the stereogenic centre of the chiral amines and amino alcohols examined in this study and the sign of the CD signal for PMAS·(amine) films. For example, although (*R*)-PhEA and (*R*)-AP each led to polymer films exhibiting a negative CD band at ca. 480 nm, so did (*S*)-CHEA and (*S*)-DMBA with the opposite configuration. However, as discussed earlier, the enantiomeric (*R*)-(+)- and (*S*)-(−)-PhEA amines gave PMAS·PhEA films with the expected mirror imaged CD spectra (Fig. 2b).

3.4. Influence of the Amine:PMAS ratio on the degree of chiral induction

The above studies employed a 1:1 amine:PMAS ratio for the aqueous mixtures used to spin cast each of the PMAS·(amine) films. This molar ratio provided one chiral amine molecule for each "free" sulfonic acid group in the PMAS dimer repeat unit. In the case of (*R*)-(+)-PhEA and (*S*)-(−)-DMBA as inducing agents, it was subsequently found that decreasing the chiral amine:PMAS dimer ratio from 1:1 to as low as 1:4 did not decrease the intensity of the optical activity observed for the spun-cast PMAS·(amine) films (see Table 2). This indicates that only one in four of the "free" sulfonate groups along the PMAS chains need to be electrostatically bound by chiral ammonium ions to achieve optimal chiral induction.

4. Conclusions

Optically active PMAS·(amine) films can be spun-cast from aqueous mixtures of PMAS with chiral amines or amino alcohols. The CD spectra of 1:1 PMAS·(amine) polymer films show Cotton effects in the visible region where the amines and amino alcohols have no electronic absorption. This confirms induction of chirality into the polymeric PMAS moiety by the incorporated amines and amino alcohols. The chiral induction is believed to be initiated by acid–base interactions with "free" sulfonic acid groups on the PMAS chains, resulting in the formation of chiral aggregates in which assemblies of PMAS chains adopt a predominantly one-handed helical arrangement. Unlike previous electrochemically deposited PMAS·(+)-PhEA and PMAS·(−)-PhEA films, the spun-cast PMAS·(amine) films do not generally exhibit bisignate character for the CD bands associated with the characteristic PMAS absorption band at 470–480 nm. This indicates the absence of exciton coupling between polaron chromophores on either the same or adjacent PMAS chains.

The secondary amine (−)-DMBA causes significantly increased chiral induction in PMAS compared to that generated by the related primary amine (−)-PhEA. The presence of bulky substituents, such as in the binaphthyl diamine (−)-BNDA, however, apparently interferes with the chiral induction and gives less optically active films. With chiral amino alcohols, the induced chirality in PMAS increases with bulkiness of the amino alcohol molecule and/or the introduction of a second chiral centre. From studies using various chiral amine:PMAS dimer molar ratios, it is found that only one in four of the "free" sulfonate groups along the PMAS chains need to be electrostatically bound by chiral ammonium ions to achieve optimal chiral induction.

The enantiomeric amines (*R*)-(+)-PhEA and (S)-(−)-PhEA generate PMAS·PhEA films with mirror imaged CD spectra, indicating the induction of opposite helical hands for the supermolecular assembly of PMAS chains. However, for structurally diverse chiral amines there is no clear correlation between the sign of the CD signals for spun-cast PMAS·(amine) films and the configuration of the amines.

Acknowledgement

The Australian Research Council is thanked for financial support.

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