

Synthesis and Chiro-Optical Properties of Water Processable Conducting Poly(diphenylamine) Nanocomposites

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Abstract: Water-soluble, chiral conducting, poly(diphenylamine) (PDPA) nanocomposites were synthesized by chemical oxidative polymerization of diphenylamine in the presence of poly(acrylic acid) (PAA) as a template and camphor sulphonic acid (CSA) as the chiral inductor. Composites were formed as stable aqueous dispersions under different experimental conditions, such as DPA to PAA molar ratios, PAA molecular weight, etc. Circular dichroism (CD) spectra of the composites indicated the induction of chirality to PDPA. Compared to simple chiral PANI, the PDPA/PAA/CSA nanocomposites showed a different Cotton effect. The appearance of a CD band in the composite was complimentary to the bisignate, exciton-coupled band in the UV-Visible spectrum. FTIR spectra indicated the intimate mixing of PDPA and PAA.

Keywords: poly(diphenylamine), poly(acrylic acid), nanocomposites.

Introduction

In biological structures such as proteins and polynucleotides, the helix of a single sense plays an important role. Many biochemical mimics are therefore developed through chemical synthesis to exploit the chirality existing in them for applications in materials science, chemical sensing and enantioselective catalysis.¹⁻⁵ It is further expected that novel applications can arise from molecular, macromolecular and supramolecular chirality. Hence, control of helicity is of the prime importance in these cases. Studies have been focused to induce macromolecular helicity through complexation with optically active compounds such as amines, acids, sugars etc.⁶⁻⁸

Chiral conducting polymers have been synthesized for potential applications to circularly polarized electroluminescence,⁹ surface modified electrodes⁹ stationary phases for chiral separations and sensors for detecting the presence of chiral molecules.¹⁰ Polyaniline (PANI), one of the most promising conducting polymers, has attracted attention for many years due to its straightforward synthesis, environ-

mental stability and potential applications in electronic devices, batteries and sensors.^{11,12} Helicity to the conjugated structure was inducted via acid-base interactions.¹³ Wallace *et al.* synthesized chiral PANI by treating the emeraldine base (EB) form of PANI with camphor sulfonic acid (CSA),¹⁴ as the chiral inductor. Films of chiral PANI were electrochemically deposited through aqueous polymerization of aniline in the presence of CSA.¹⁵ Processability of the chiral PANI was improved through the preparation of water-soluble PANI nanocomposites by electrochemical polymerization of aniline in the presence of CSA and a dispersant (typically polystyrene sulfonate or colloidal silica).¹⁶ A self-doped water-soluble chiral polyaniline derivative was prepared by the electrochemical polymerization of 2-methoxyaniline-5-sulfonic acid in the presence of CSA¹⁷ chiral deoxyribonucleic acid (DNA)/PANI intertwined complex was prepared by employing DNA as chiral template.¹⁸

Similar to chiral PANI, chiral poly(o-methoxyaniline) (PMAO) has been prepared with the use of two alternative procedures, one involving the enantioselective electrochemical polymerization of o-methoxyaniline in the presence of CSA,¹⁹ and the other by post-protonation of EB form of POMA with (+) or (-) CSA in an organic solvent.²⁰

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Wang *et al.*^{21,22} reported the synthesis of water soluble chiral PANI nanocomposites using CSA as chiral inducing agent and poly(acrylic acid), PAA, as the template. The chirality of PAA/PANI/CSA was induced by the chiral dopant, CSA and the composite retained optical activity even after the removal of the chiral agent. In that template-guided synthesis, a complex formation between aniline, PAA, and CSA is attributed to cause chirality. However, studies on the optical activity of *N*-substituted PANIs are rare.

Among the PANI class, poly(diphenylamine) PDPA, a polymer of *N*-aryl substituted aniline, has attracted now-a-days.²³⁻³³ Many properties of PDPA²⁷⁻³³ that include electrochemistry, conductivity, luminescence and electrochromism are found to be different from PANI and also from polymers of other *N*-substituted aniline derivatives. Gopalan *et al.*^{25,26,29-33} reported the details of electrochemistry, spectro-electrochemistry, optical properties and thermal behaviour by PDPA. In the recent studies,^{27,28} attempts have been made to incorporate newer properties into PDPA by grafting a non-conducting polymer onto its backbone. However, to our knowledge, a study related to the chiral induction in PDPA has not been reported so far.

This paper reports on the template guided synthesis of PDPA nanocomposites. The synthesis involves chemical oxidative polymerization of a PAA/diphenylamine (DPA) complex in the presence of a chiral inducing agent, CSA. PAA was used as the template to induce processability to PDPA. Experimental parameters like molecular weight of the polyelectrolyte and concentration of monomer (DPA) were altered to probe the influence of the conditions on chiral induction in PDPA. Chiro-optical properties of the nanocomposites were investigated by circular dichroism (CD) spectro-polarimetry and UV-visible spectroscopy.

Experimental

Materials. Poly(acrylic acid) (PAA) (10,000 MW or 250,000 MW), camphor sulfonic acid [(-) CSA] and diphenylamine were purchased from Sigma-Aldrich, USA. Ammonium persulfate (APS) (Merck, USA) and aniline (Oriental chemical Industries, Korea) were used as received.

Synthesis of Chiral Poly(diphenylamine). A typical procedure is outlined below: a solution consisting of 10 mL DPA (0.0011 mol) and PAA (0.0022 mol, monomer unit; 250,000 Mw) was prepared. The solution was stirred overnight to form DPA/PAA adduct. 1 mL of 3 M (-) CSA was slowly added drop wise to the above solution with stirring for 1 h. 1 mL of ammonium persulfate, APS (0.01 M) was added drop wise to the above mixture. The mixture was further stirred for 24 h at 4°C. A dark green coloration was seen indicating the formation of PDPA/PAA/CSA, in which PDPA existed in its doped form.²⁴⁻²⁷ The PDPA/PAA/CSA composites were precipitated by adding ethanol and filtered. The precipitate was dried in vacuum for 24 h at 80°C. The

nanocomposites were also prepared for under different experimental conditions.

Neutralization of Doped Chiral Poly(diphenylamine). PDPA/PAA/CSA composite was treated with aqueous ammonia for 24 h. The solution turned to blue in that process. The neutralized composite of PDPA/PAA/CSA was precipitated by the addition of ethanol, filtered and dried at 80°C.

Analytical Techniques. Transmission electron micrographs of the composites were obtained using a Phillips CM-30 transmission electron microscope (TEM) operating at 300 kV. Samples for TEM analysis were prepared by evaporating of a drop of the solution onto a 300 mesh carbon copper grid. Circular dichroism (CD) spectra were collected on a JascoJ-750 spectropolarimeter with a scan rate of 200 nm/min. Samples were prepared by filling the quartz cell (2 nm path length) with the diluted nanocomposites aqueous solution. The signal was then averaged out after five scans. UV-Visible spectrum of the composite was recorded using Shimadzu UV-Visible spectrometer. Fourier transform (FT-IR) spectra of PAA and DPA mixture and the composites of DPA (doped and neutral) were recorded from a Matson Galaxy series FT-IR 50001 spectrometer a Bruker IFS 66V FT-IR spectrometer.

Results and Discussion

Morphology of PDPA/PAA/CSA Nanocomposite. TEM images of as synthesized PDPA/PAA/CSA nanocomposite and the components of the composites, DPA, (-) CSA and PAA are presented (Figure 1). Before polymerization, the ingredients (DPA/PAA and CSA) were present with a large size distribution. However, PDPA/PAA/CSA nanocomposite consists of fairly a narrow size distributed nanometer sized spherical beads.

Chiro-optical Properties of PDPA/PAA/CSA Nanocomposite. The CD spectra (Figure 2) of aqueous solution (green colored) of PDPA/PAA/CSA show that optical activity is induced in PDPA for the composites prepared under different experimental conditions. CD spectra of PDPA/PAA/CSA nanocomposites show a peak at 290 nm, and another band around 570 nm. CSA does not show any CD bands beyond 300 nm.^{34,35} Hence, the CD bands at the wavelength longer than 300 nm is attributed to the induced optical activity in PDPA. The composites, PAA/PDPA/CSA, prepared with different concentration of DPA, molecular weight of PAA and optical forms of CSA [(+) or (-)] show optical activity arising from the conducting polymer, PDPA (Figure 2). And, there are variations in optical activities depending on the conditions of making the composite. It is important to know the origin of optical induction in PDPA by considering the reasons of already reported chiral induction to PANI (as PDPA is a polymer of *N*-phenyl substituted PANI). The observed CD bands for PDPA are quite different

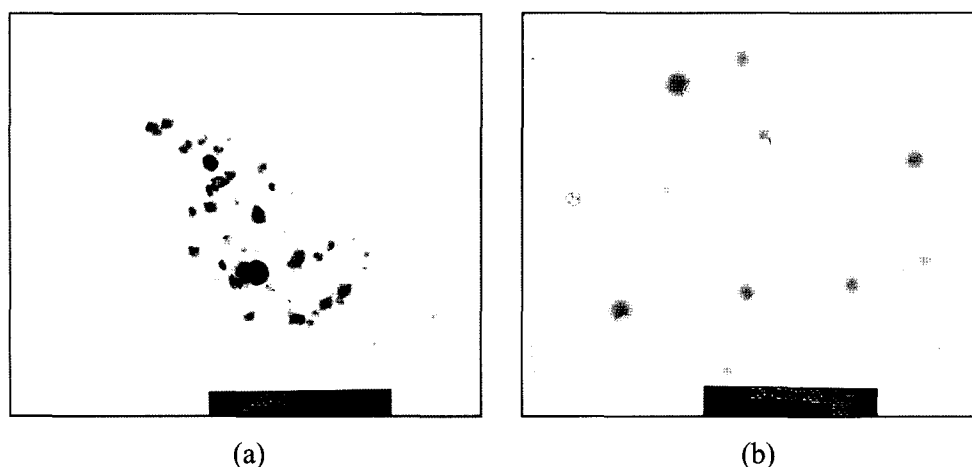


Figure 1. Transmission electron micrograph of the reaction mixture consisting of PAA, DPA and (-) CSA (a) before polymerization and (b) PDPA/PAA/CSA nanocomposite.

from the ones reported for PANI.³⁶⁻³⁸ The difference in optical induction between PDPA and PANI can therefore be considered not simply as a substituent effect that has been observed for several chiral substituted anilines.^{39,41} We envisage that the structural differences between PDPA and PANI would be the reason for the difference in optical activity.

PANI possesses leucoemeraldine, emeraldine and pernigraniline as main redox states arising from C-N coupled structure.^{40,41} On the contrary, PDPA has benzidine type repeat units because of C-C-phenyl-phenyl coupled structure.^{29,33} Diphenosemiquinonimino imine and diphenoquinondiimine forms are possible for PDPA as the polaronic and bipolaronic states in PDPA.^{23,29,33} These structures make PDPA in an entirely different electronic states in contrast to PANI.^{29,33,34}

For PANI/CSA system, the observed CD band around 440 nm has been assigned as bisignate, exciton coupled bands associated with polaron transition.^{34,38} Induced optical activity by CSA has been explained through macromolecular asymmetry arose from PANI chain adopting preferred one-side helical screw that was reported to be maintained by enantiomeric CSA anions linking NH^+ and NH center in the dimeric repeat units in PANI chain. The chiral anions (CSA-) were visualized to attach to the PANI through electrostatic bonding of sulfonate ion in CSA to the NH^+ centre and H bonding of carbonyl group of CSA to NH sites.³⁴⁻³⁸ For PAA/PANI/CSA system, results revealed that CSA though induces helicity in PANI, the chiral conformation is memorized in PANI/PAA composite through intertwined complexation of PANI with PAA.²²

For our system, it is clear that there is induced chirality in PDPA (Figure 2). We envisage that the oxidized states of PDPA form inter macromolecular complex with PAA and forced PDPA into one sided helical structure through hydrogen bonding interaction between carbonyl group of PAA and $-\text{NH}^+$ group in PDPA. This hypothesis was supported

from FT-IR spectroscopy.

Figure 3 represents the FT-IR spectrum of the composites, PAA/PDPA/(-) CSA and PAA/PDPA. The PDPA/PAA composite was prepared by mixing neutralized PDPA with PAA to understand the probable interactions between the groups in PAA and PDPA. On comparison of the IR spectrum of PDPA/PAA/(-)CSA and PAA (neutral)/PDPA and pure neutral PDPA, we noticed that all the bands observed for pure PDPA get shifted. Besides that, there is significant change in the intensity of band corresponding to carbonyl peak of

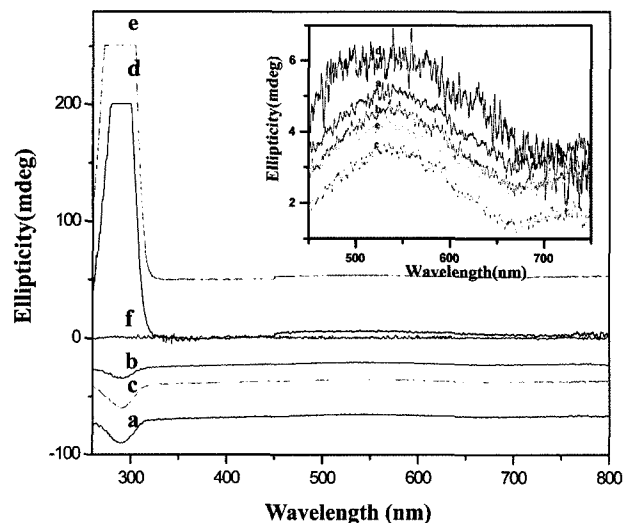


Figure 2. CD spectra of PAA/PDPA/CSA composites prepared under different experimental conditions (a-f): DPA = 0.0011 M (a, c, e), 0.0028 M (b,d), PAA = (250,000 MW) = 0.0022 M (a, b, e), PAA (10,000 MW) = 0.0022 M (c, d), (-) CSA = 3 M (a, b, c), (+) CSA = 3 M (d, e), APS = 0.01 M (a-c, e), 0.02 M (d) and (f) DPA = 0.0011 M, PAA = (250,000 MW) = 0.055 M, APS = 0.01 M.

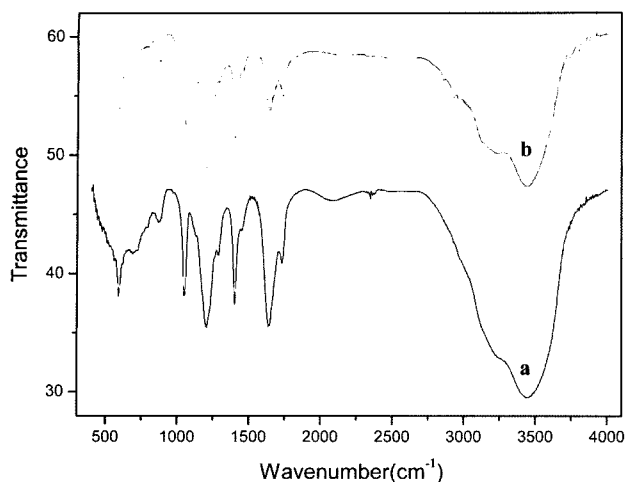


Figure 3. FT-IR spectrum of PAA/PDPA/(-) CSA composite (a), PAA/PDPA composite (b). a: composite prepared with PAA (250,000 MW) = 0.0022 M, DPA = 0.0011 M, APS = 0.01 M, (-) CSA = 3 M, b: composite prepared by mixing 0.1 g of neutralized PDPA with 0.16 g of PAA (250,000 MW).

PAA and -C=N- stretch of PDPA. These two observations clearly suggest that there can be molecular level interaction between the groups of PDPA and PAA. For example, FT-IR spectra of PDPA^{26,34} shows band for aromatic secondary amine NH- bonding around for 1491 cm^{-1} , C-H out of plane bending vibration of para substituted benzene rings at 850 cm^{-1} , benzenoid type ring stretching around 1500 cm^{-1} and quinoid ring stretching around 1600 cm^{-1} and C-H bending vibration of diphenoquinoneimine type units around 1170 cm^{-1} . The band positions of the vibrational modes in the FT-IR spectrum (Figure 3) of PAA/PDPA are found to be shifted in comparison to PDPA. Clearly, there are variations in the relative intensities of carbonyl stretch and quinoid stretch band between the PAA/PDPA and PAA/PDPA/(-)CSA. Obviously, there can be interactions between the carbonyl of PAA groups and groups in quinoid form of phenyl ring in PDPA to alter the relative intensities of these two bands. The spectrum of PAA/PDPA/(-)CSA composite has pronounced quinoid ring stretching band (1600 cm^{-1}) in comparison to PAA/PDPA. This informs that there can be additional hydrogen bonding interactions between C=O group in CSA and -NH groups in PDPA. The conductivity of the PAA/PDPA composite was $\sim 10^{-4}$ S/cm which lower than pristine PDPA probably due to the presence of insulating PAA.

The composites, PAA/PDPA/CSA, were prepared with different optical forms of chiral agent, CSA. The CD spectra of the PAA/PDPA/(+)CSA and PAA/PDPA/(-)CSA composites are presented in Figures 2(d) and 1(c). Interestingly, irrespective of the optical form of chiral inducing agent used, (+) CSA or (-) CSA, the chiral induction in PDPA is unaffected. The CD spectrum (Figure 2) shows a

band around 570 nm that is consistent with the 'excitonic' band noticed in UV-Visible spectra of these composites (Figure 4). It informs that only one-sided helical conformation could be preferentially induced in PDPA. This is contrast to the results observed for PANI/(+)CSA and PANI/(-)CSA systems.^{38,40} Positive and negative cotton effects have been noticed for PANI/(+)CSA and PANI/(-)CSA.³⁶ Acid doping of emeraldine base form of poly(o-methylaniline) and PMOA with (+) or (-)CSA resulted chirality but the intensity of CD bands was much weaker than parent PANI.⁴⁰ This was considered due to steric hindrance to polymer rearrangements by methyl or methoxy substituent. Similarly, poly(ethoxyaniline) could not show optical activity because of the large steric hindrance of bulky ethoxy substituent that prevents the possible hydrogen bonding interchain of CSA with NH site in substituted PANI. This makes it to have one side screw with (+) or (-) CSA.⁴⁰ In the case *N*-(alkylamines), the higher steric hindrance of *N*-substituted alkyl groups, could induced helical structure with preferred one screw conformation.⁴³ It is to be noted that these conjugated polymers show optical activity due to the induced helical structure even though the polymer contains no configurationally chiral group in the side or main chain.³⁷⁻⁴⁰ If the helix formed is a dynamic one, helix reversal or twist can occur along the chain even at the room temperature.⁴¹ The helical structures and helix senses in the formed polymer are expected to be influenced by the conditions used for the polymerization, formation and stabilization of the helical structure, thermodynamically or kinetically, during polymerization, extend of interactions between the chiral inductor and the groups in the main or side chain of the polymer.⁴²⁻⁴⁶ Based on the data, the helix formation is often explained by speculative schemes.^{37,46-48} Such analyses and discussions are still on debate. In the absence of concrete experimental evidences for the structure at a single molecule level, it becomes to difficult to explain many observations.⁴²⁻⁴⁶

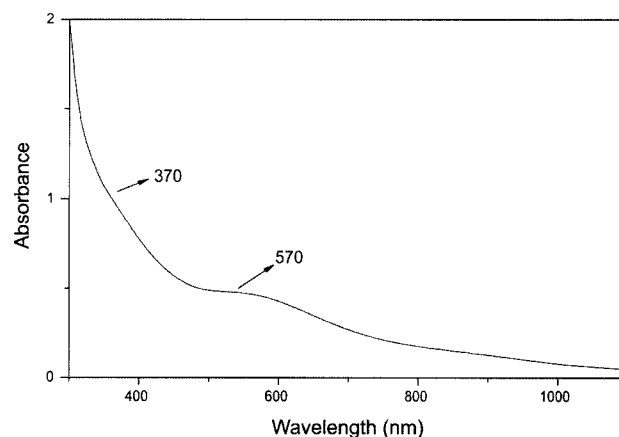


Figure 4. UV-Visible spectrum of PDPA/PAA/CSA nanocomposite.

UV-Visible spectrum of PDPA/PAA/CSA nanocomposite (Figure 4) shows a shoulder around 370 nm and a broad band around 570 nm. These bands correspond to the oxidized polaronic and bipolaronic form of PDPA, respectively.^{25,26,29,32} The observed CD band (570 nm) for PDPA (Figure 2) is now assigned for the exciton coupled bipolaronic band. The composites prepared with different molecular weights of PAA (250, 000 Mw and 10,000 Mw) show optical activity.

It is important to know the origin of chiral induction in PDPA by considering the reasons of already reported for chiral induction to PANI (as PDPA is a polymer of *N*-phenyl substituted PANI). The observed CD bands for PDPA are quite different from the ones reported for PANI.⁴⁹⁻⁵² The difference in optical induction between PDPA and PANI cannot be ascribed simply due to the substituent effect.⁵³⁻⁵⁶ We envisage that the differences in the electronic states and structures between PDPA and PANI would be the reason for the difference in chiro-optical properties for PDPA in comparison to PANI.

PANI possesses leucoemeraldine, emeraldine and pernigraniline as main redox states arising from C-N coupled structure.⁵⁷⁻⁵⁹ On the contrary, PDPA, has benzidine type repeat units because of the C-C-phenyl-phenyl coupled structure. Diphenosemiquinonamino imine and diphenoquinondiimine structural forms correspond to the polaronic and bipolaronic states in PDPA.^{23,28,31} These structures of PDPA contribute to different electronic states to PDPA in contrast to PANI.^{25,28,31}

For PANI/CSA system, a CD band has been noticed around 440 nm and assigned as the bisignate exciton coupled band associated with polaronic transition.^{34,36-39} Induced optical activity to PANI by CSA has been explained through macromolecular asymmetry arose from PANI chain adopting preferred one-side helical screw. It has been reported that CSA anion interacts with NH⁺ and NH units in PANI to induce helical structure. The chiral anions (CSA⁻) interact with PANI through electrostatic bonding of sulfonate ion in CSA to the NH⁺ sites at PANI and also through H-bonding interactions between carbonyl group of CSA and NH sites of PANI.^{34,36-39} It has been reported that for the PANI/PAA/CSA composite CSA induces helicity to PANI and the chiral conformation is memorized in PANI/PAA composite through the inter-winned complexation of PANI with PAA.²² The composites, PDPA/PAA/CSA, showed an electrical conductivity in the order of 10⁻³ S/cm, which is three order higher than neutral PDPA.

In the present study, induced chirality in PDPA (Figure 2) is explained as follows. PDPA forms inter-macromolecular complex with PAA through molecular interactions described in the literature.^{22,34,36-39} Hence, one sided helical structure for PDPA is possible through hydrogen bonding interactions between carbonyl groups of PAA and -NH⁺ groups in PDPA.^{22,34,36-39}

After ascertaining the reasons for chiral induction in

PDPA and optical activity of PDPA/PAA/CSA nanocomposite through CD spectrum, we wanted to ensure the stage of chiral induction to PDPA. Chirality in PDPA can be induced *in situ* during polymerization or after the formation of PDPA through interactions with chiral inducing agent, CSA. We made few studies to understand this. There was no change in the intensity of the CD band (CD spectrum not shown) on further addition of (-) CSA to the formed composite PDPA/PAA/(-) CSA. Also, the removal of chiral dopant (-) CSA by neutralization from the composite does not influence the intensity of CD band. This indicates that chirality was not influenced by post polymerization treatment. There was no chiral induction if PDPA was prepared separately and doped subsequently with (+) or (-) CSA. Hence, it is presumed that chirality is induced in PDPA only during polymerization.

The chiro-optical properties of the composites, PDPA/PAA/CSA prepared under different experimental conditions were followed. The composites, PDPA/PAA/CSA prepared with different molecular weights of PAA show optical activity (Figure 2). Comparatively, optical of PDPA/PAA/CSA prepared with PAA of 10,000 Mw is lower in comparison to composite prepares with PAA of 250,000 Mw. The variations of intensity in CD band (Figure 2) may arise due to the difference in the concentration of PDPA in the optically active conformation. Otherwise, changes in molecular weight of PAA influence the extent of PDPA to transform into the optically active form.

Conclusions

Template guided synthesis can be used induce chirality in poly(diphenylamine), PDPA. Aqueous dispersion of chiral PDPA can be obtained in the form of water-processable composite. The composite can be prepared under various experimental conditions. Chirality in PDPA was induced during polymerization. The molecular interactions between the template, PAA and PDPA seem to be the determining factor for the chiral induction in PDPA. The optically active water processable composite of PDPA find application as a modifier in the capillary electrophoresis and be used for enatio separations.

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References

- (1) D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, **95**, 2725 (1995).
- (2) L. Pu, *Acta Polym.*, **48**, 116 (1997).

- (3) Y. Okamoto and E. Yashima, *Angew. Chem. Int. Ed. Engl.*, **37**, 1922 (1998)
- (4) M. M. Green, *Topics in Stereochemistry*, Materials- Chirality, John Wiley & Sons Inc., 2003, Vol. 24.
- (5) K. Tang, M. M. Green, K. S. Cheon, J. V. Selinger, and B. A. Garetz, *J. Am. Chem. Soc.*, **125**, 7313 (2003).
- (6) E. Yashima, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **117**, 11596 (1995).
- (7) E. Yashima, T. Nimura, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **118**, 9800 (1996).
- (8) E. Yashima, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **119**, 6345 (1997).
- (9) B. J. Rault, E. Raoult, H. J. Tahri, D. H. Le, and J. Simonet, *Electrochim Acta*, **44**, 3409 (1999).
- (10) (a) J. C. Moutet, E. Saintaman, F. Tranvan, P. Angibeaud, and J. P. Utille, *Adv. Mater.*, **4**, 511 (1992), (b) X. Chen and Y. Okamoto, *Macromol. Res.*, **15**, 134 (2007).
- (11) (a) J. Jang, J. Ha, and S. Kim, *Macromol. Res.*, **15**, 154 (2007), (b) J. Jang, J. Ha, and S. Kim, *Macromol. Res.*, **15**, 154 (2007).
- (12) J. Y. Kwon, E. Y. Kim, and H. D. Kim, *Macromol. Res.*, **12**, 303 (2004).
- (13) S. A. Ashraf, L. A. P. KaneMaguire, M. R. Majidi, S. G. Pyne, and G. G. Wallace, *Polymer*, **38**, 2627 (1997).
- (14) M. R. Majidi, L. A. P. Kane-Maguire, and G. G. Wallace, *Polymer*, **36**, 3597 (1995).
- (15) M. R. Majidi, L. A. P. Kane-Maguire, and G. G. Wallace, *Polymer*, **35**, 3113 (1994).
- (16) V. Aboutanos, J. N. Barisci, L. A. P. Kane-Maguire, and G. G. Wallace, *Synth. Met.*, **106**, 89 (1999).
- (17) E. V. Strounina, L. A. P. Kane-Maguire, and G. G. Wallace, *Synth. Met.*, **106**, 129 (1999).
- (18) R. Nagarajan, W. Liu, J. Kumar, S. K. Tripathy, F. Bruno, L. A. Samuelson, *Macromolecules*, **34**, 3921 (2001).
- (19) I. D. Norris, L. A. P. Kane-Maguire, and G. G. Wallace, *Macromolecules*, **33**, 3237 (2000).
- (20) I. D. Norris, L. A. P. Kane-Maguire, G. G. Wallace, and L. H. C. Mattoso, *Aust. J. Chem.*, **53**, 89 (2000).
- (21) P. A. McCarthy, J. Y. Huang, S. C. Yang, and H. L. Wang, *Langmuir*, **18**, 259 (2002).
- (22) L. Wenguang, A. M. Patrick, L. Dingguo, H. Jianyu, C. Y. Sze, and L. W. Hsing, *Macromolecules*, **35**, 9975 (2002).
- (23) L. Y. Guo and K. Noriyuki, *Macromolecules*, **36**, 7939 (2003).
- (24) J. Guay, R. Paynter, and L. H. Dao, *Macromolecules*, **23**, 3598 (1990).
- (25) C. Y. Chung, T. C. Wen, and A. Gopalan, *Electrochimica Acta*, **47**, 423 (2001).
- (26) V. Rajendran, A. Gopalan, T. Vasudevan, and T. C. Wen, *J. Electrochem. Soc.*, **147**, 3014 (2000).
- (27) F. Hua and E. Ruckenstein, *Langmuir*, **20**, 3954 (2004).
- (28) F. Hua and E. Ruckenstein, *Macromolecules*, **36**, 9971 (2003).
- (29) M. Thanneermalai, T. Jeyaraman, C. Sivakumar, A. Gopalan, T. Vasudevana, and T. C. Wen, *Spectrochimica Acta Part A*, **59**, 1937 (2003).
- (30) P. Santhosh, M. Sankarasubramanian, M. Thanneermalai, A. Gopalan, and T. Vasudevan, *Mater. Chem. Phys.*, **85**, 316 (2004).
- (31) Y. T. Tasi, T. C. Wen, and A. Gopalan, *Sens Actuators B*, **B96**, 646 (2003).
- (32) P. Santhosh, T. Vasudevan, and A. Gopalan, *Spectrochim Acta A*, **59**, 1427 (2003).
- (33) M. S. Wu, T. C. Wen, and A. Gopalan, *J. Electrochem. Soc.*, **148**, D65 (2001).
- (34) E. E. Havuiga, M. M. Bouman, E. W. Meiger, A. Pop, and M. M. Simenon, *Synth. Met.*, **66**, 93 (1994).
- (35) I. D. Norris, L. A. P. Kane-Maguire, and G. G. Wallace, *Macromolecules*, **31**, 6529 (1998).
- (36) K. A. Piaso, S. Kaneko, K. Sakamoto, H. Shirakawa, and M. Kyotami, *Science*, **27**, 1683 (1998).
- (37) K. Maeda, K. Morino, Y. Okamoto, T. Sato, and E. Yashima, *J. Am. Chem. Soc.*, **126**, 4329 (2004).
- (38) M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, and S. Lifson, *Science*, **268**, 1860 (1995).
- (39) T. Nakano and Y. Okamoto, *Chem. Rev.*, **101**, 4013 (2001).
- (40) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, and N. A. J. M. Sommerdijk, *Chem. Rev.*, **101**, 4039 (2001).
- (41) K. Shinohara, S. Yasuda, G. Kato, M. Fujita, and H. Shigekawa, *J. Am. Chem. Soc.*, **123**, 3619 (2001).
- (42) Y. Okamoto, M. Matsuda, T. Nakano, and E. Yashima, *J. Polym. Sci.; Part A: Polym. Chem.*, **32**, 309 (1994).
- (43) K. Maeda, M. Matsuda, T. Nakano, and Y. Okamoto, *Polym. J.*, **27**, 141 (1995).
- (44) M. Muller and R. Zentel, *Macromolecules*, **29**, 1609 (1996).
- (45) M. M. Andreola, C. Munoz, B. Reidy, and M. P. Zelo, *J. Am. Chem. Soc.*, **110**, 4063 (1988).
- (46) M. Inouye, M. Waki, and H. Abe, *J. Am. Chem. Soc.*, **126**, 2022 (2004).
- (47) M. Ishikawa, K. Maeda, and E. Yashima, *J. Am. Chem. Soc.*, **124**, 7448 (2002).
- (48) D. Berthier, T. Buffeteau, J. M. Leger, R. Oda, and I. Huc, *J. Am. Chem. Soc.*, **124**, 13486 (2002).
- (49) D. M. Tigellar, W. Lee, K. A. Wates, A. J. Saprigin, V. N. Prigodin, X. Cao, L. A. Nafie, M. S. Platz, and A. Epstein, *J. Chem. Mater.*, **14**, 1430 (2002).
- (50) J. Huang, V. M. Egan, H. Guo, J. Y. Yoon, A. L. Briseno, I. E. Rauda, R. L. Garrel, C. M. Knobler, F. Zhou, and R. B. Kanee, *Adv. Mater.*, **15**, 1158 (2003).
- (51) A. Aboutanos, J. N. Barisci, L. A. P. Kane-Maguire, and G. G. Wallace, *Synth. Met.*, **106**, 89 (1999).
- (52) S. J. Su and N. Kuramoto, *Macromolecules*, **34**, 7269 (2001).
- (53) S. J. Su and N. Kumaranto, *Chem. Mater.*, **34**, 7249 (2001).
- (54) V. S. Ekaterina, L. A. P. Kane-Maguire, and G. G. Wallace, *Synth. Met.*, **106**, 129 (1999).
- (55) K. A. Runcie and R. J. K. A. Taylor, *Macromolecules*, **3**, 3237 (2001).
- (56) G. L. Yuan and N. Kuramoto, *Macromolecules*, **35**, 9773 (2002).
- (57) A. Pud, N. Ogurtsov, A. Korzhenko, and L. G. Shapova, *Prog. Polym. Sci.*, **28**, 1701 (2003).
- (58) N. Gospodinova and L. Terlemezyan, *Prog. Polym. Sci.*, **23**, 1443 (1998).
- (59) W. S. Huang and A. G. MacDiarmid, *Polymer*, **34**, 1833 (1993).