

Electrically Conductive Nanocomposites of Polyaniline with Poly(vinyl alcohol) and Methylcellulose

Dipankar Chattopadhyay, Mrinal Kanti Bain

Department of Polymer Science and Technology, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata 700009, India

Received 23 February 2008; accepted 14 May 2008

DOI 10.1002/app.28836

Published online 2 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electrically conductive nanocomposites of HCl-doped polyaniline (PANI-HCl) nanocolloid particles with water-soluble and film-forming polymers such as poly(vinyl alcohol) (PVA) and methylcellulose (MC) were prepared by the redispersion of preformed MC-coated submicrometric PANI-HCl particles in PVA and MC solutions under sonication for 1 h and the casting of the films from the dispersions followed by drying. The submicrometric polyaniline (PANI) particles were prepared by the oxidative dispersion polymerization of aniline in an acidic (1.25M HCl) aqueous ethanol (30 : 70) medium with MC as a steric stabilizer. The particles contained 4.7 wt % MC and had a conductivity of 7.4 S/cm. They had an oblong

shape of 203 nm (length) and 137 nm (breadth). Sonication broke the oblong-shaped particles to sizes of ~ 10 nm in the PVA matrix and ~ 60 nm in the MC matrix. The electrical conductivity of these films was measured, and the percolation threshold was determined. The composites had the characteristics of a low percolation threshold at a volume fraction of PANI of 2.5×10^{-2} in the PVA matrix and at a volume fraction of 3.7×10^{-2} in the MC matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2849–2853, 2008

Key words: conducting polymers; nanocomposites; water-soluble polymers

INTRODUCTION

Intrinsically conductive polymers, particularly polyaniline (PANI), have potential use in a large number of applications such as transparent conductive coatings, electromagnetic shielding, antistatic formulations, light-emitting diodes, and corrosion-resistant paints. However, most conducting polymers suffer from processing difficulties because of their inherent insolubility and infusibility. Among conductive polymers, PANI has received great attention because of its environmental stability and low cost. PANI doped with hydrochloric acid prepared chemically by oxidative polymerization cannot be processed by conventional plastic processing techniques such as extrusion molding and injection molding because the polymer is insoluble and infusible. Wessling and coworkers,^{1–3} however, reported the preparation of HCl-doped polyaniline (PANI-HCl) in a more uniform and pure state that flows at 100–250°C; this makes it possible to blend it with conventional polymers. The reported percolation threshold (f_p) occurred at a 0.035 volume fraction of PANI, which was much lower than the theoretical f_p value of 0.16 predicted by percolation theory for statistical blends.⁴

Several other methods used to make PANI processable include N substitution^{5,6} or ring substitution^{7–9} of aniline, doping the PANI base with functionalized protonic acid,^{10,11} and making colloidal particles of PANI by dispersion polymerization.^{12–19} PANI dispersions can be used for the processing of PANI, including the preparation of microstructured electrically conducting composite films composed of PANI. Thus, the synthesis of colloidal particles of PANI and their application to making conducting composites with film-forming polymers have attracted great interest.^{20–22} Gospodnova et al.²² used colloidal PANI-dodecylbenzenesulfonic acid (DBSA) dispersions for the preparation of blends with water-soluble poly(vinyl alcohol) (PVA) and water-insoluble ethylene/vinyl acetate host polymers. The blends thus obtained exhibited an f_p value lower than 0.5 wt % in both cases. Banerjee and Mandal^{20,21} reported blends of PANI-HCl colloid particles with a number of common vinyl polymers with f_p in the range of 2.5×10^{-4} to 4×10^{-4} . These extremely low values of f_p have been attributed to the formation of unstable nanoparticles of PANI-HCl from the breakdown of colloidal PANI-HCl particles with the application of ultrasound and subsequent fractal assembly of the nanoparticles. Heeger and coworkers^{23–25} reported a blend of camphor sulfonic acid doped PANI with poly(methyl methacrylate) with an f_p value as low as 10^{-2} . According to them, the low value of f_p was

Correspondence to: D. Chattopadhyay (dipankar.chattopadhyay@gmail.com).

due to the self-assembly of PANI/camphor sulfonic acid molecules during liquid-liquid phase separation.

Narkis et al.²⁶ reported blends of PANI-DBSA aqueous dispersions with aqueous emulsions of matrix polymers, such as polystyrene, poly(methyl methacrylate), and polyacrylate. These blends exhibited electrical conductivity at a very low PANI-DBSA content (0.5 wt %). According to them, the conductivity level of the various blends depended on the PANI content and on the surfactant present in the polymer matrix emulsion, and it was practically independent of the nature of the polymeric matrix.

Zhang et al.²⁷ reported the synthesis of composite films of nanostructured PANI (nanotubes or nanorods 60–80 nm in diameter) with water-soluble PVA. Recently, Hino et al.²⁸ synthesized novel conducting composites of PANI prepared in the presence of sodium dodecyl sulfonate and several water-soluble polymers. According to them, the corresponding composites had good film-forming properties and showed good conductivity close to 32 S/cm.

Yang et al.²⁹ synthesized blends of oligomeric PANI with an epoxy resin to form an interpenetrating network. The cured film was doped by being dipped into an acetic acid solution of *p*-toluene sulfonic acid. According to them, the PANI/epoxy resin composites showed a very low threshold concentration of *o*-PANI (lower than 1 part of *o*-PANI per 100 parts of resin) for electrical conduction.

In this work, the electrical conductivity of composites of submicrometric colloidal PANI particles prepared with methylcellulose (MC) as a steric stabilizer in a 70 : 30 alcohol/water medium with PVA and MC is reported. Of the two matrices that we have chosen, PVA is partially compatible with the steric stabilizer MC, and the other matrix is the same as the steric stabilizer. The composites have the characteristics of low f_p values at a volume fraction of 2.5×10^{-2} in the PVA matrix and at a volume fraction of 3.7×10^{-2} in the MC matrix. A study of the morphology of the nanocomposites is also included.

EXPERIMENTAL

Purification of the reagents and chemicals

Aniline (E. Merck, Mumbai, India) was vacuum-distilled over zinc metal; the middle fraction was collected and stored under argon at -10°C . MC was a product of British Drug Laboratories and was used as received. We determined a degree of substitution of 1.7 and a viscosity-average molecular weight of 4.3×10^5 for it. PVA was purchased from LOBA Cheme Pvt., Ltd. (Mumbai, India). Commercial

distilled water was redistilled over alkaline permanganate. Ethyl alcohol (Bengal Chemical and Pharmaceutical Works, India) was purified with the method of Danner and Hildebrand.³⁰ It was then fractionally distilled with a 1-m fractionating column packed with 3-mm porcelain beads. Ammonium persulfate (E. Merck, Germany) was used as received.

Polymer synthesis and preparation of the composites

The PANI colloid particles were prepared by the oxidative dispersion polymerization of aniline in an aqueous ethanol (70%) medium containing 1.25M HCl with ammonium persulfate as the initiator and MC as the steric stabilizer at 2°C . The molar ratio of aniline to persulfate was kept at 1. The aniline/stabilizer ratio was 1.5 : 1, and the stabilizer concentration was maintained at 0.5%. PANI colloid particles were separated by ultracentrifugation. Composites were prepared by the redispersion of PANI colloid particles in PVA and MC solutions in a conical flask with an ultrasonic cleaning bath (model AU 10C, Eyela, Japan) with a power of 60 W that was operated at 28 kHz.

Polymer and composite characterization

Dried particles of PANI were pelletized, and the conductivity was measured with the standard four-probe method with a constant direct-current source (model 224, Keithley) and a nanovoltmeter (model 181, Keithley, Germany). Transmission electron microscopy (TEM) studies were performed on diluted dispersions dried on carbon-coated copper grids with a JEOL JEM 100CP electron microscope. The N content of PANI was estimated with a semimicro Kjeldahl technique.³¹

RESULTS AND DISCUSSION

The successful dispersion polymerization of aniline with MC as a steric stabilizer cannot be performed in water.^{32,33} Our research results have shown that MC can be effectively used as a steric stabilizer for the dispersion polymerization of aniline if the medium is changed from water to aqueous ethanol.¹⁵

A stable PANI dispersion was obtained when the polymerization was carried out in a 70 : 30 alcohol/water medium with MC as a stabilizer. The morphology of the particles is shown in Figure 1. The morphology was determined with TEM. The particles were oval-shaped and had dimensions of 203 ± 26 nm (length) and 137 ± 24 nm (breadth) (Fig. 1).

The stability of a dispersion depends on the rate of stabilizer adsorption and the rate of particle

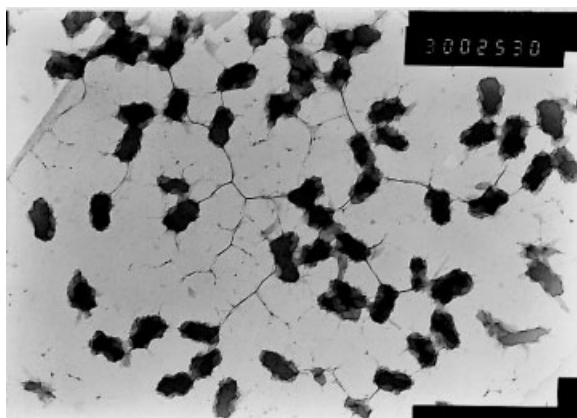


Figure 1 TEM image of PANI-MC colloid particles prepared in 70% ethanol (magnification = 30,000 \times).

growth (the rate of polymerization).^{13,32} A spherical shape is produced when the balance is in the favor of the former.³² The change from a spherical shape to an oblong shape arises as the balance increasingly tilts in favor of the latter. In an aqueous ethanol medium, the rate of aniline polymerization decreases.¹⁷ Therefore, the rate of adsorption of the MC stabilizer exceeded the rate of polymerization in an aqueous ethanol medium, and the result was oblong-shaped colloid particles of PANI. PANI colloid particles were separated by ultracentrifugation and used for composite preparation with PVA and MC via ultrasound.

The changes in the room-temperature conductivity of composite films of PVA and MC are shown in Figures 2 and 3, respectively. As Figures 2 and 3 do

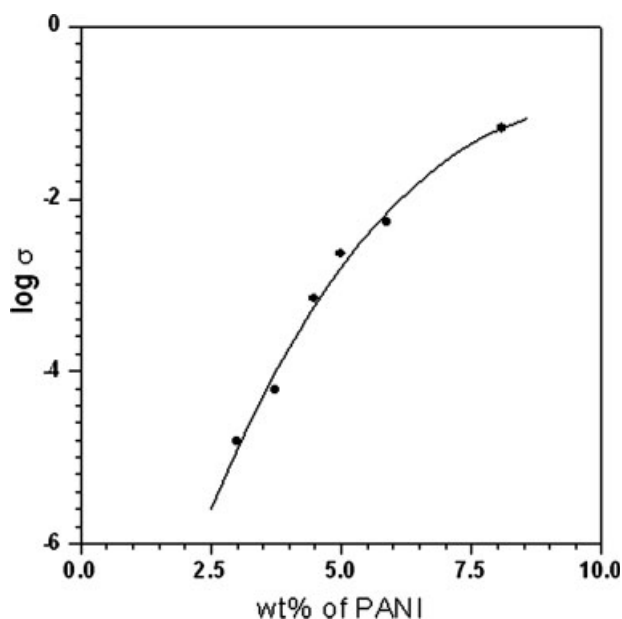


Figure 2 Variation in the electrical conductivity ($\log \sigma$) against the PANI-HCl concentration in the PANI-HCl/PVA composites.

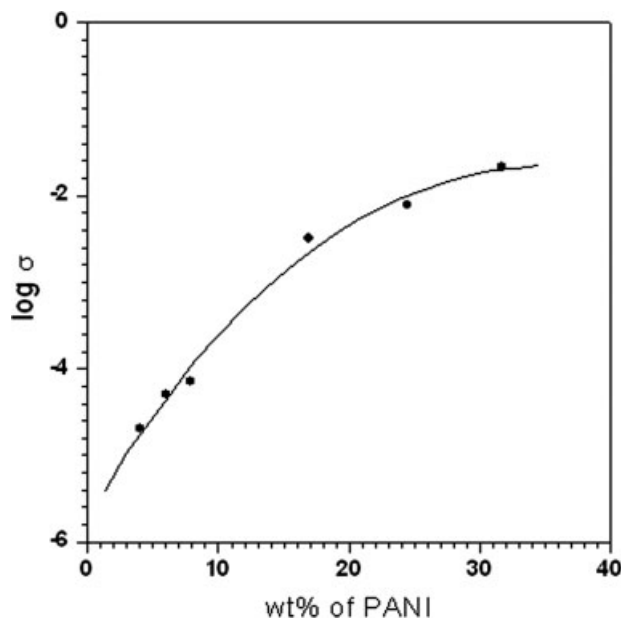


Figure 3 Variation in the electrical conductivity ($\log \sigma$) against the PANI-HCl concentration in the PANI-HCl/MC composites.

not show any well-defined f_p value, the data were fitted to the following scaling law of percolation theory^{4,34} in Figures 4 and 5:

$$\sigma(f) = c(f - f_p)^t$$

where c is a constant, t is the critical exponent, and f_p is the volume fraction of the filler particles. By fitting our experimental data to this scaling law, as shown in Figures 4 and 5, we estimated the critical

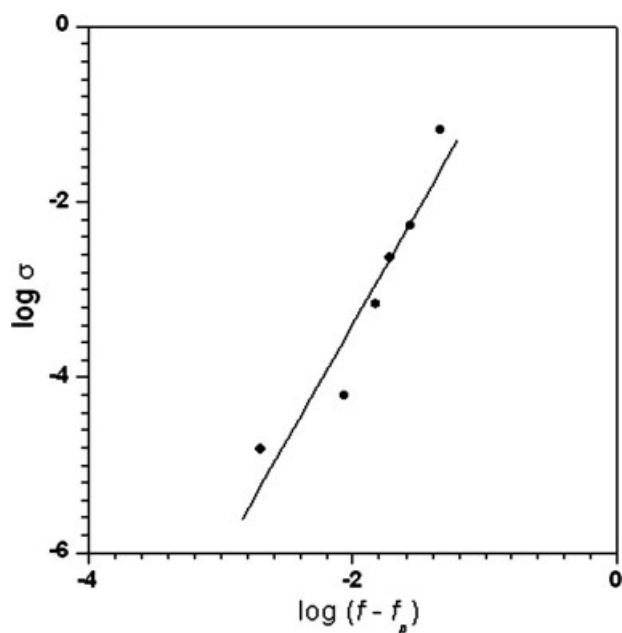


Figure 4 Variation in $\log \sigma$ against $\log(f - f_p)$ in the PANI-HCl/PVA composites.

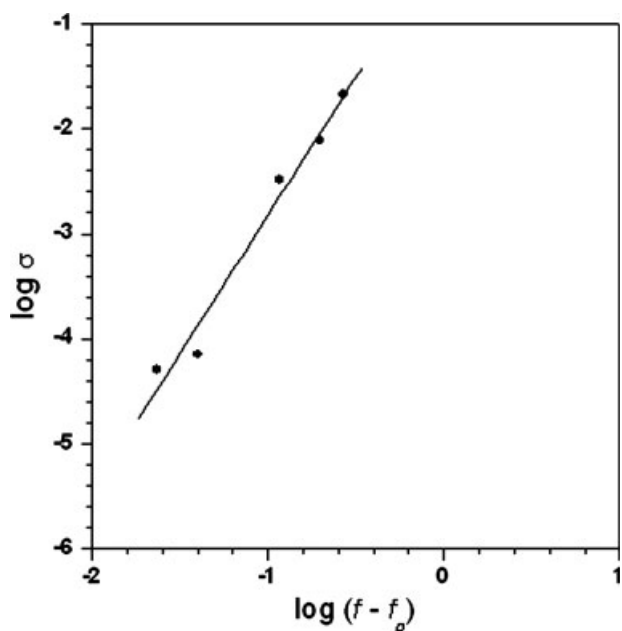


Figure 5 Variation in $\log \sigma$ against $\log(f - f_p)$ in the PANI-HCl/MC composites.

f_p values of a 0.023 volume fraction for the PANI-HCl/PVA composite and a 0.033 volume fraction for the PANI-HCl/MC composite. These values were much lower than the theoretical predicted value of $f_p = 0.16$ for spherical conducting particles dispersed in a nonconducting matrix in three dimensions.⁴ From the slopes of the straight lines shown in Figures 4 and 5, the values of t were determined to be 2.01 for the PANI-HCl/PVA composite and 3.13 for PANI-HCl/MC. Earlier, Yang and Rubner³⁵ reported a low f_p value ($f_p = 0.028$) and a value of $t = 3.2$ for a semi-interpenetrating network of poly(3-octylthiophene) and divinylbenzene-crosslinked polystyrene.

The morphology of the PANI colloid particles and composites was established with TEM. The PANI particles were originally oval-shaped and had dimensions of 203 ± 26 nm (length) and 137 ± 24 nm (breadth) (Fig. 1). Figures 6 and 7 present the morphology of the blends of PANI-HCl with PVA and MC just above f_p , that is, 3.73 wt % for PVA and 6.06 wt % for MC.

The low value of f_p compared to the theoretical value of $f_p = 0.16$ (for spherical particles) in both cases was due to the breakdown of MC-stabilized PANI colloid particles to nanoparticles under sonication during the preparation of the composites and subsequent formation of the network structure. The MC-PANI colloid particles had dimensions of 203×137 nm² (Fig. 5), whereas the particles forming the network structures (Figs. 6 and 7) were a few nanometers in size (10–60 nm). Thus, it is clear that under the application of ultrasound, the oblong MC-

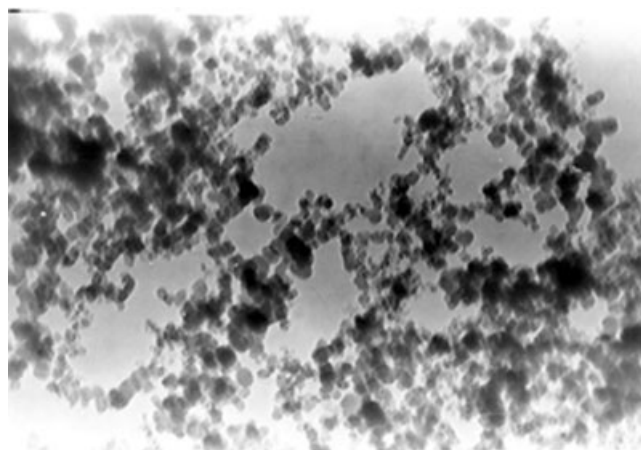


Figure 6 TEM image of the PANI-HCl/PVA composite films containing 3.73 wt % PANI-HCl (magnification = 60,000 \times).

PANI particles broke into nanoparticles and formed a network structure at a low volume percentage of PANI. The values of f_p observed in the PVA and MC matrices were almost the same. This observation is similar to the earlier observation made by Narkis et al.²⁶ that f_p is independent of the polymer matrix. We observed that although the f_p values were the same in both matrices, a 0.069 volume fraction of the PANI-HCl particles was required to reach a conductivity level of the order of 10^{-2} S/cm in the PVA matrix, whereas a 0.3 volume fraction of the PANI-HCl particles was required in the case of the MC matrix. The reason for this observation may be that the steric stabilizer MC, which adsorbed onto the PANI-HCl particles, was partially compatible with the PVA matrix but completely miscible with the MC matrix. Thus, the formation of a network structure due to aggregation was more effective when the matrix polymer was not completely miscible with the steric stabilizer, and the effect was more

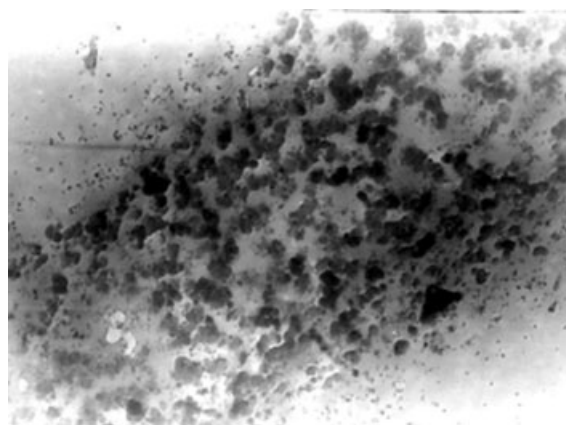


Figure 7 TEM image of the PANI-HCl/MC composite films containing 6.06 wt % PANI-HCl (magnification = 25,000 \times).

pronounced at a higher loading of PANI particles covered with the MC steric stabilizer. Thus, a lower volume fraction of PANI particles coated with the MC stabilizer was required to reach a conductivity level of 10^{-2} S/cm in the case of the PVA matrix versus the MC matrix.

CONCLUSIONS

Several nanocomposites of PANI-HCL colloid particles with water-soluble film-forming polymers such as PVA and MC were prepared by the redispersion of MC-coated PANI-HCL nanoparticles in PVA and MC solutions with ultrasound for 1 h in a sonicator bath and the casting of the films from dispersions. The submicrometric colloid particles were synthesized by the oxidative dispersion polymerization of aniline in an aqueous ethanol (30 : 70) medium with MC as a steric stabilizer. The composites showed low f_p values at a volume fraction of PANI of 2.5×10^{-2} in the PVA matrix and at a volume fraction of 3.7×10^{-2} in the MC matrix. Finally, although the volume fraction of PANI needed to reach f_p was nearly the same for both types of matrices, the volume fraction required to reach a high conductivity (10^{-2} S/cm) for the PVA matrix was significantly lower than that required for the MC matrix.

The authors gratefully acknowledge the experimental support from the Technical Education Quality Improvement Programme (TEQUIP) project, Government of India. One of the authors (M.K.B.) thanks University Grants Commission (UGC), Government of India, for his fellowship under the University Potential for Excellence (UPE) scheme.

References

- Wessling, B.; Valk, H. *Synth Met* 1986, 16, 127.
- Wessling, B.; Valk, H. *Synth Met* 1987, 18, 671.
- Wessling, B.; Valk, H.; Mathew, N. R.; Kulkarni, V. G. *Mol Cryst Liq Cryst* 1988, 160, 205.
- Stauffer, D. *Introduction to Percolation Threshold*; Taylor & Francis: London, 1985.
- Chevalier, J.-W.; Bergeron, J.-Y.; Dao, L. H. *Polym Commun* 1989, 30, 308.
- Watanabe, A.; Mori, K.; Iwabuchi, A.; Iwasaki, Y.; Nakamura, Y.; Ito, O. *Macromolecules* 1989, 22, 3521.
- Leclere, M.; Gauay, J.; Dao, L. H. *Electroanal Chem* 1988, 251, 21.
- Leclere, M.; Gauay, J.; Dao, L. H. *Macromolecules* 1989, 22, 649.
- Wei, Y.; Focke, W. W.; Wenk, G. E.; Ray, A.; Mac-Diarmid, A. G.; Akhtar, M.; Kiss, Z.; Epstein, A. *J Phys Chem* 1989, 93, 495.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1993, 55–57, 3514.
- Armes, S. P.; Aldissi, M.; Agnew, S.; Gottesfeld, S. *Langmuir* 1990, 6, 1745.
- Drarmitt, C.; Armes, S. P. *J Colloid Interface Sci* 1992, 150, 134.
- Stejskal, J.; Kratochvil, P.; Helmstedt, M. *Langmuir* 1996, 12, 3389.
- Chattapadhyay, D.; Mandal, B. M. *Langmuir* 1996, 12, 1585.
- Chattapadhyay, D.; Banerjee, S.; Chakravorty, M.; Mandal, B. M. *Langmuir* 1998, 14, 1544.
- Chattapadhyay, D.; Chakravorty, M.; Mandal, B. M. *Polymer Int* 2001, 50, 538.
- Stejskal, J. *Polym Mater* 1997, 18, 27.
- Stejskal, J. In *Dendrimers, Assemblies, Nanocomposites*; Arshady, R.; Guyot, A., Eds.; Citus: London, 2002; p 195.
- Banerjee, P.; Mandal, B. M. *Synth Met* 1995, 74, 257.
- Banerjee, P.; Mandal, B. M. *Macromolecules* 1995, 28, 3940.
- Gospodinova, N.; Mokreva, P.; Tsanov, T.; Terlemezyina, L. *Polymer* 1997, 38, 743.
- Yang, C. Y.; Coa, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1993, 53, 293.
- Reghu, M.; Yoon, C. O.; Yang, C. Y.; Moses, D.; Heeger, A. J.; Cao, Y. *Macromolecules* 1993, 26, 7245.
- Reghu, M.; Yoon, C. O.; Yang, C. Y.; Moses, D.; Smith, P.; Heeger, A. J.; Cao, Y. *Phys Rev B* 1994, 50, 13931.
- Haba, Y.; Segal, E.; Narkis, M.; Titleman, G. I.; Siegmann, A. *Synth Met* 2000, 110, 189.
- Zhang, Z.; Meixiang, W. *Synth Met* 2002, 128, 83.
- Hino, T.; Namiki, T.; Kuramoto, N. *Synth Met* 2006, 156, 1327.
- Yang, X.; Zhao, T.; Yu, Y.; Wei, Y. *Synth Met* 2004, 142, 57.
- Danner, P. S.; Hildebrand, J. H. *J Am Chem Soc* 1922, 44, 2824.
- Cole, J. O.; Parks, C. R. *Ind Eng Chem* 1946, 18, 61.
- Armes, S. P.; Aldissi, M. *J. Chem Soc Chem Commun* 1989, 88.
- Vincent, B.; Waterson, J. *J. Chem Soc Chem Commun* 1990, 683.
- Zallen, R. *The Physics of Amorphous Solids*; Wiley: New York, 1983; Chapter 4.
- Yang, Y.; Rubner, M. F. *Macromolecules* 1992, 25, 3284.