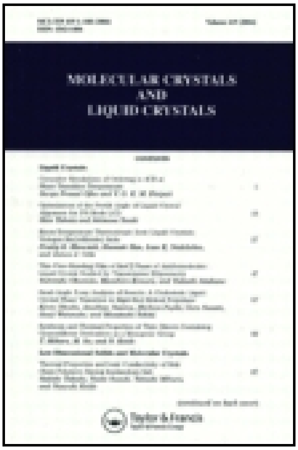

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Conjugated Polyaniline Nanorod Blends with Cyanoresin

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To cite this article: Ji Hyoung Choi, Seong Hun Kim & Kyung Wha Oh (2007): Conjugated Polyaniline Nanorod Blends with Cyanoresin, Molecular Crystals and Liquid Crystals, 464:1, 281/[863]-289/[871]

To link to this article: http://dx.doi.org/10.1080/15421400601031256

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 281/[863]–289/[871], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601031256

Conjugated Polyaniline Nanorod Blends with Cyanoresin

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Polyaniline nanorods (PANI-NR) were synthesized by the template free method. The diameter and length of PANI-NR was approximately $120 \sim 200\,nm$ *and* $600 \sim 1200\,nm$*, respectively. PANI-NR/cyanoresin blends were prepared by the addition of cyanoresin/dimethylformamide (DMF) solutions to PANI-NR/DMF solutions. The conductivity of PANI-NR/cyanoresin blends was in the range of* $10^{-3} \sim 10^{-1}\,S/cm$ *depending on the cyanoresin content. Thermal stability of PANI-NR/cyanoresin blend was improved with increasing cyanoresin content.*

Keywords: conducting polymer; cyanoresin; nanorod; polyaniline

1. INTRODUCTION

Conducting polymers such as polyaniline (PANI), polypyrrole and poly (3,4-ethylenedioxythiophene) have been widely investigated because of their extensive applications in electronic industry such as secondary batteries, capacitors etc [1–4]. In general, PANI has various advantages including easy of synthesis, doping character, cost-effectiveness, environmental stability and the conducting polymers with nanostructures are promising for high conductive materials [5,6].

Template synthesis is a common and effective method to synthesize conducting polymers with nanostructures [7–9]. However, template

This work was supported by the Korea Science and Engineering Foundation Grant funded by the Korean Government (Grant No. R01-2005-000-10850-0).

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removal process is needed from synthesized nanotubes or nanowires in the template method. Therefore, it is particularly interesting to form nanostructures by self-assembly process. Recently, Wan *et al.* [10–12] introduced a template free method, termed as an in-situ doping polymerization in the presence of β-naphthalene sulfonic acid (β-NSA) as a dopant to synthesize microtubes of PANI. It was proposed that the formation of these PANI microtubes could result from the salt formation of aniline with the self-assembled β-NSA molecules [12], where β-NSA molecule acts as both a supermolecular template [13] and a self-doping agent. There have been several reports about the dopant-dependent morphology of PANI such as porous [14], rod-like [15], needle-like [16], fiber [17] and tube [18] shapes.

In this research, PANI nanorods (PANI-NR) were synthesized with p-toluenesulfonic acid (TSA) and camphoresulfonic acid (CSA) as the dopants by template free method. PANI doped with TSA was reported insoluble in organic polar solvents. In contrast, cyanoresin has an excellent solubility in organic solvents and ease of film fabrication. Furthermore, cyanoresin cast film is highly transparent and exhibits good mechanical properties [19]. Therefore, it is expected that poor processability and thermal stability of PANI-NR can be greatly improved by blending it with cyanoresin. PANI-NR and cyanoresin blends were prepared by *in situ* blending method. Morphology and conductivity of PANI-NR/cyanoresin blends prepared with different dopant types and blend compositions were studied.

2. EXPERIMENTAL

Synthesis of PANI-NR

Aniline monomer (Sigma Aldrich) was distilled under reduced pressure. Cyanoresin (Shin-Etsu Chemical Co.) and other regents were used as received without further treatment. PANI-NRs were synthesized by the template free method with ammonium persulfate (APS) as an oxidant and TSA or CSA as the dopant. Typical synthesis process of PANI-NR was as follows: aniline monomer (0.04 mol) was mixed with 200 ml of distilled water containing dopant (0.02 mol) with stirring at room temperature and the mixture solution was kept in a cooling bath at −2°C. APS (0.04 mol) dissolved in 100 ml of distilled water was added slowly to the above mixture solution over a period of 30 min and the polymerization was carried out for 15 hrs −2°C. Resulting PANI was filtered at reduced pressure, washed with deionized water, methanol and ethyl ether several times and dried at room temperature *in vacuo* for 24 hrs. In order to investigate effect of the dopant concentration on the characteristics of PANI, PANI with different monomer to dopant molar ratio (aniline monomer: dopant: oxidant = 1:2:1) was also synthesized.

PANI-NR/Cyanoresin Blends

The PANI-NR/cyanoresin blends were prepared by *in situ* blending method. Cyanoresin used in this study was a copolymer of cyanoethyl-pullulan and cyanoethyl-poly(vinyl alcohol) with molar ratio of 1:1. Cyanoresin/DMF solution was added to PANI-NR/DMF solution with stirring at room temperature for 24 hrs.

Characterizations

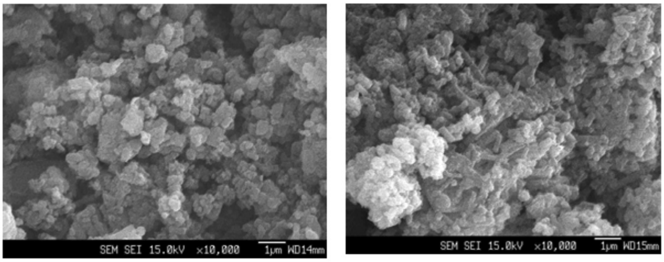
Conductivity of PANI-NR/cyanoresin blends was measured by a four-probe technique with a Keithly 238 high-current-source measuring unit at room temperature. Fourier transform infrared (FT-IR) spectra of PANI, PANI-NR, PANI-NR/cyanoresin blends were recorded with Nicolet 760 Magna IR spectrometer with KBr disc technique and their morphologies were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F) and transmission electron microscopy (TEM, Hitachi-530). Thermogravimetric analysis (TGA) of PANI, cyanoresin and PANI-NR/cyanoresin blends was carried out in a Pyris 1 thermogravimetric analyzer (Perkin Elmer) under nitrogen atmosphere from 30 to 700°C at a heating rate of 10°C/min.

3. RESULTS AND DISCUSSION

Effects of Kind and Concentration of Dopant on Morphologies

The morphologies of synthesized PANI powders prepared with different dopants and dopant concentrations are shown in Figure 1(a), (b) and (c). Morphology PANI (TSA) powder prepared with molar ratio of 1:2:1 (aniline monomer: dopant: oxidant) is shown in Figure 1(a), exhibiting spherical shape. On the other hand, morphologies of PANI-NR (TSA) and PANI (CSA) synthesized with molar ratio of 1:0.5:1 (aniline monomer: dopant: oxidant) were rod-like as shown in Figure 1(b) and (c), respectively. From the different morphologies of PANI (TSA) and PANI-NR, it was found that the nanorod formation is affected by the concentration of dopant and that the morphology of PANI is also controlled by dopant type used in polymerization. In TEM image of Figure 1(d), the diameter and length of PANI-NR (TSA) were approximately 120 nm and 600 nm, respectively.

(a) PANI (TSA) (b) PANI-NR (CSA)



(c) PANI-NR (TSA) (d) PANI-NR (TSA)

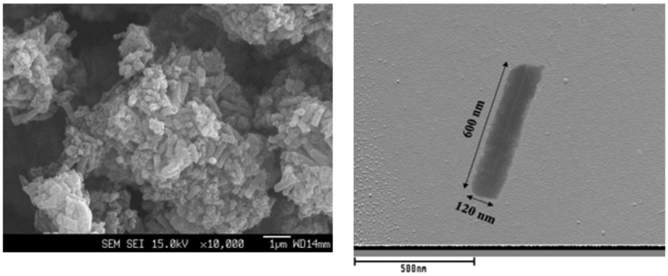


FIGURE 1 FE-SEM images of (a) PANI (TSA), (b) PANI-NR (CSA), (c) PANI-NR (TSA) and (d) TEM image of PANI-NR (TSA).

PANI-NRs synthesized with different dopants were blended with cyanoresin of different compositions by *in situ* blending method. In PANI-NR (TSA)/cyanoresin blends, it was conformed that organic solvent had little effect on the morphology of PANI-NR (TSA) and that PANI-NR (TSA) were well blended with the cyanoresin. However, the morphology of PANI-NR (CSA) was affected significantly by the presence of organic solvent since PANI doped with CSA has good solubility in organic solvents. Therefore, we used PANI-NR (TSA)/cyanoresin blends for further research.

Chemical Structures of PANI-NR, Cyanoresin and their Blend

FT-IR spectra of PANI-NR (TSA), cyanoresin and PANI-NR (TSA)/cyanoresin blends are displayed in Figure 2. PANI-NR (TSA) showed characteristic peaks for quinoid ring C=N=C stretching (1560 cm^{-1}), benzonoid ring C–N–C stretching (1490 cm^{-1}), aromatic C–N stretching (1310 cm^{-1}), secondary C–N stretching (1290 cm^{-1}). The absorption peak of at 3400 cm^{-1} in cyanoresin spectrum is assigned to the hydroxyl (O–H) group, which is not observed in the

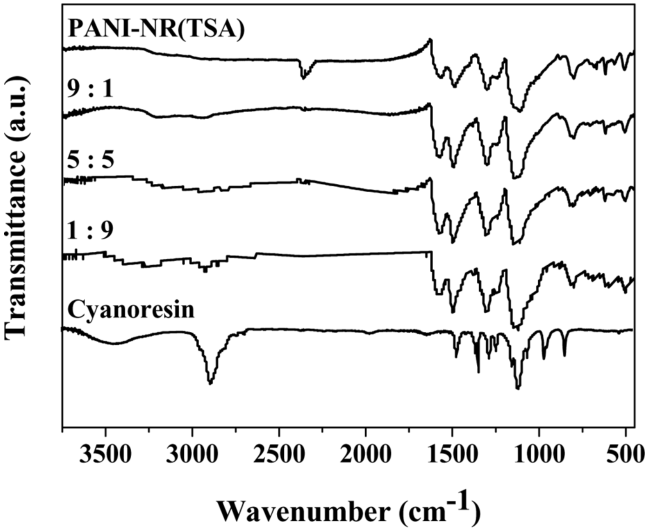


FIGURE 2 FT-IR spectra of PANI-NR (TSA), cyanoresin and PANI-NR (TSA)/cyanoresin blends.

spectrum of PANI-NR (TSA). PANI-NR (TSA)/cyanoresin blend (blend ratio = 1:9) showed a peak at approximately 3290 cm^{-1}, which is shifted from the absorption peak of pure cyanoresin. In general, non-hydrogen bonded O−H stretching vibration is observed at 3600 cm^{-1}, while broad hydrogen bonded O−H stretching vibration is observed from 3400 to 3200 cm^{-1}. Therefore, the peak shift of the blends indicates that the cyanoresin forms intermolecular hydrogen bonding with PANI-NR (TSA).

Conductivity and Thermal Stability of PANI-NR (TSA)/ Cyanoresin Blends

Electrical conductivities of PANI (TSA), PANI-NR (TSA) and their blends are shown in Figure 3, exhibiting higher conductivity of PANI-NR (TSA) than that of PANI (TSA). In general, conductivity of conducting polymer is affected by the concentration of dopant used during synthesis [20]. As the concentration of dopant increased, the growth of chains is interrupted, resulting in shortening chain length. Therefore, conductivity is decreased with decreased conducting path length. Since PANI (TSA) was synthesized with higher molar ratio of dopant than PANI-NR (TSA), PANI-NR (TSA) possesses higher conductivity value than PANI (TSA). Another possible interpretation is

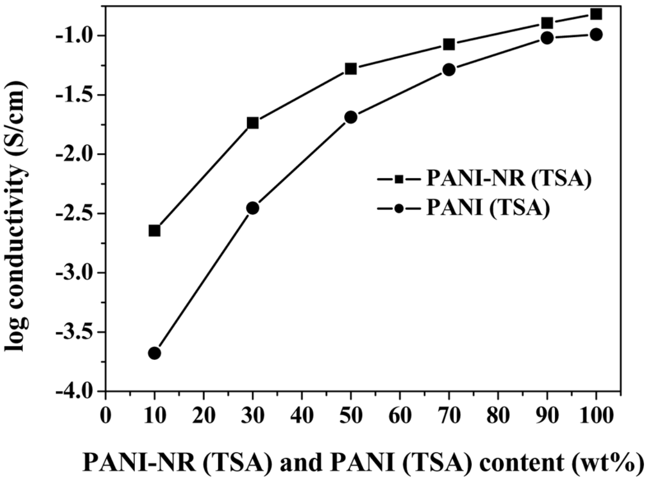


FIGURE 3 Conductivity of PANI (TSA)/cyanoresin and PANI-NR (TSA)/cyanoresin blends.

their morphological difference. As shown in Figure 1(a) and (c), PANI-NR (TSA) showed uniform morphology, while PANI (TSA) did not show uniformity for their morphology. Therefore, it is thought that PANI-NR (TSA) has higher conductivity caused by more uniform conducting path.

PANI-NR (TSA)/cyanoresin blends exhibited higher conductivity than PANI (TSA)/cyanoresin blends at same PANI contents, certainly because of higher conductivity of PANI-NR (TSA). Conductivity of PANI-NR (TSA)/cyanoresin blends was in the range of $10^{-3} \sim 10^{-1}$ S/cm at room temperature and the conductivity of the blend decreased with increasing cyanoresin content as shown in Figure 3.

However, as shown in Figure 4, it was observed that PANI-NR (TSA) showed better thermal stability than PANI (TSA) and that thermal stability was improved with increasing cyanoresin content. In the thermogram of PANI-NR (TSA), the first weight loss was observed from 50 to 110°C, due to the loss of water molecule [21]. The second weight loss occurred between 250 and 355°C, possibly because of the loss of unbound dopant molecules from the PANI-NR (TSA) chain [22]. The third decomposition step region (355 ~ 580°C) indicated the degradation of polymeric chain for PANI-NR (TSA) [23]. The final step (above 580°C) indicated the decomposition of backbone and ring-opening of benzene for PANI-NR (TSA) [23]. In the thermogram of cyanoresin, almost one-step weight loss of main chain was observed between 400 and 440°C. The PANI-NR (TSA)/cyanoresin blends

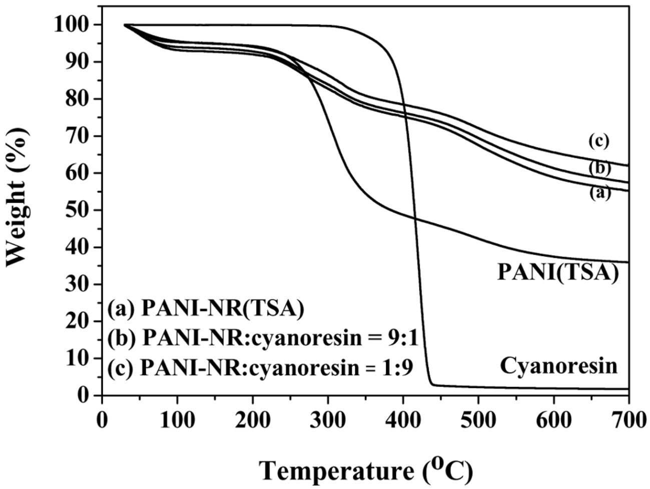


FIGURE 4 TGA thermograms of PANI (TSA), PANI-NR (TSA), cyanoresin and PANI-NR (TSA)/cyanoresin blends.

showed almost same decomposition behaviors of the PANI-NR (TSA). However, residual weight percentage of the blends increased with increasing cyanoresin content, because of enhanced hydrogen bonding between PANI-NR (TSA) and cyanoresin.

Analysis of thermal degradation stability was performed by Doyle's method [24] and the integral procedural decomposition temperature (IPDT) was calculated as follows:

$$\mathrm{IPDT}\,(^{\circ}\mathrm{C}) = A^{*}K^{*}(T_f - T_i) + T_i \tag{1}$$

where, A^{*} is the area ratio of the total experimental curve divided by the total TGA thermogram, K^{*} is the coefficient of A^{*}, T_i is the initial experimental temperature (°C) and T_f is the final experimental temperature (°C). As listed in Table 1, PANI-NR (TSA) exhibited higher

TABLE 1 Thermal Stability Parameters for PANI (TSA), PANI-NR (TSA), Cyanoresin and PANI-NR (TSA)/Cyanoresin Blends

Sample (Dopant: TSA)	A^{*}	K^{*}	$A^{*}K^{*}$	IPDT (°C)
PANI	0.599	1.095	0.656	469.6
PANI-NR	0.737	1.118	0.824	582.1
Cyanoresin	0.492	1.005	0.494	361.2
PANI-NR/cyanoresin (9:1)	0.752	1.121	0.843	594.8
PANI-NR/cyanoresin (1:9)	0.778	1.128	0.878	618.3

IPDT value than PANI (TSA) and the cyanoresin had the lowest IPDT value. However, cyanoresin exhibited the highest thermal stability up to 400°C in the TGA thermograms. Moreover, the PANI-NR (TSA)/cyanoresin blends had higher IPDT values than the PANI (TSA), PANI-NR (TSA) and cyanoresin. These results indicate that the hydrogen bonding between PANI-NR (TSA) and cyanoresin existed and thermal stability of PANI-NR (TSA) was improved by cyanoresin.

CONCLUSIONS

PANI-NR was prepared by the template free method with different dopant types, observing that formation of PANI-NR was affected by molar ratio of dopant and that morphology of PANI was also controlled by dopant used in polymerization. The diameter and length of PANI-NR (TSA) were approximately 120 nm and 600 nm, respectively. From the O-H absorption peak shift of PANI-NR (TSA)/cyanoresin blends, it was also confirmed that intermolecular hydrogen bonding was formed between PANI-NR (TSA) and cyanoresin. PANI-NR (TSA) showed higher conductivity than PANI (TSA) and the conductivity of PANI-NR (TSA)/cyanoresin blends was in the range of $10^{-3} \sim 10^{-1}$ S/cm depending on cyanoresin content. Thermal stability was improved with increasing cyanoresin contents because of the formation of hydrogen bonding between PANI-NR (TSA) and cyanoresin.

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