

## Reply to “Comment on ‘Preparation and Characterization of Silver–Poly(vinylidene fluoride) Nanocomposites: Formation of Piezoelectric Polymorph of Poly(vinylidene fluoride)’”

Swarup Manna and Arun K. Nandi\*

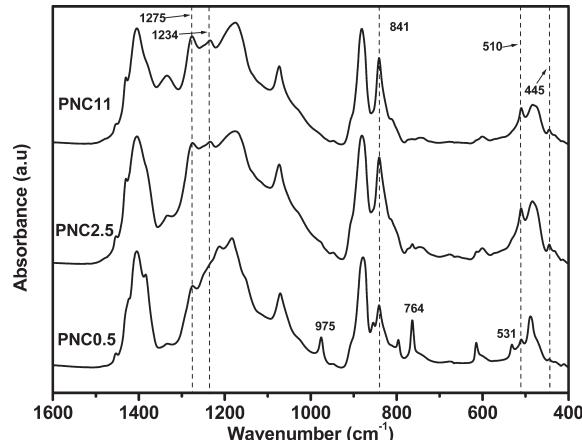
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

We note that the arguments advanced by us in ref 1 for identification of the  $\beta$ -polymorph of poly(vinylidene fluoride) (PVDF) have been used earlier by many authors.<sup>2–5</sup> The main objection of Mandal et al.<sup>6</sup> to the said method of identification of the  $\beta$ -polymorph hinges on the absence of a distinct peak at  $1279\text{ cm}^{-1}$  in the FTIR spectra (Figure 7) of the composites.<sup>1</sup> Actually, in the reported spectra, there is a hump at  $\sim 1279\text{ cm}^{-1}$  for every composite sample. Due to the saturation absorbance (as pointed out by Mandal et al.<sup>6</sup>), the hump could not be resolved into a distinct peak and accordingly it was not reported in Table 2 of our paper.<sup>1</sup> We have now repeated our experiment<sup>1</sup> and recorded FTIR spectra of films of very low thickness, thereby avoiding the problem of saturation absorption. The spectra of the three composites are presented in Figure 1. We note that the characteristic peaks of  $\beta$ -phase PVDF, e.g.,  $1275$ ,  $841$ ,  $510$ , and  $445\text{ cm}^{-1}$ , are now observed in each of the samples (PNC0.5, PNC2.5, and PNC11).<sup>5,7,8</sup> The  $1279\text{ cm}^{-1}$  peak is slightly red-shifted and appears at  $1275\text{ cm}^{-1}$ , invalidating the main objection of Mandal et al.<sup>6</sup> We have, therefore, strong reasons to claim that our reported method<sup>1</sup> of Ag/PVDF nanocomposite preparation induces the  $\beta$ -phase PVDF formation in the composites.

The  $1234\text{ cm}^{-1}$  peak is present in our old as well as new samples and is attributed to the TT sequence.<sup>7,8</sup> It should accordingly be observed in both  $\beta$ - and  $\gamma$ -polymorphs.<sup>9</sup> The  $841$  and  $510\text{ cm}^{-1}$  vibrational peaks are also common to both  $\beta$ - and  $\gamma$ -polymorphs.<sup>7,8</sup> For the  $\gamma$ -polymorph, the characteristic vibrational peaks arise from the  $T_3G$  sequences at  $776$ ,  $811$ ,  $1115$ , and  $1134\text{ cm}^{-1}$ .<sup>7–10</sup> These peaks are not observed at all in any of our previously reported or newly made samples. Thus, there is no ambiguity that only the  $\beta$ -polymorph is produced in our method of Ag/PVDF composite formation.<sup>1</sup> It should be pointed out here that a mixture of  $\alpha$  ( $975$ ,  $764$ ,  $531\text{ cm}^{-1}$ ) and  $\beta$  ( $1275$ ,  $840$ ,  $510\text{ cm}^{-1}$ ) polymorphs is produced in the new PNC0.5 sample due to the low concentration of Ag nanoparticles (AgNP), for its inability to crystallize the whole PVDF sample in the all-trans conformation of  $\beta$ -PVDF.

Reports of a higher ( $5$ – $10\text{ }^\circ\text{C}$ ) melting point of the  $\beta$ -phase compared to that of the  $\alpha$ -phase PVDF are not rare in the literature.<sup>2,3,11,12</sup> However, Gianellis and his co-workers have observed almost the same melting point for the  $\beta$ - and  $\alpha$ -phase.<sup>4</sup> In this context, our DSC data does not contradict  $\beta$ -phase formation, as the melting peaks are higher by  $2$ – $3\text{ }^\circ\text{C}$  than those of  $\alpha$ -phase PVDF.<sup>1</sup>

The formation of  $\beta$ -PVDF in our method<sup>1</sup> is further supported from the lack of birefringence in the samples due to random orientations of the crystallites.<sup>4,11</sup> In the polarized optical micrographs (Figure 2) of the new PNC 0.5 sample,



**Figure 1.** FTIR spectra of newly prepared Ag/PVDF nanocomposite thin films at indicated compositions (the preparation conditions are the same as reported in ref 1). The dotted lines identify the characteristic peaks of  $\beta$ -PVDF.

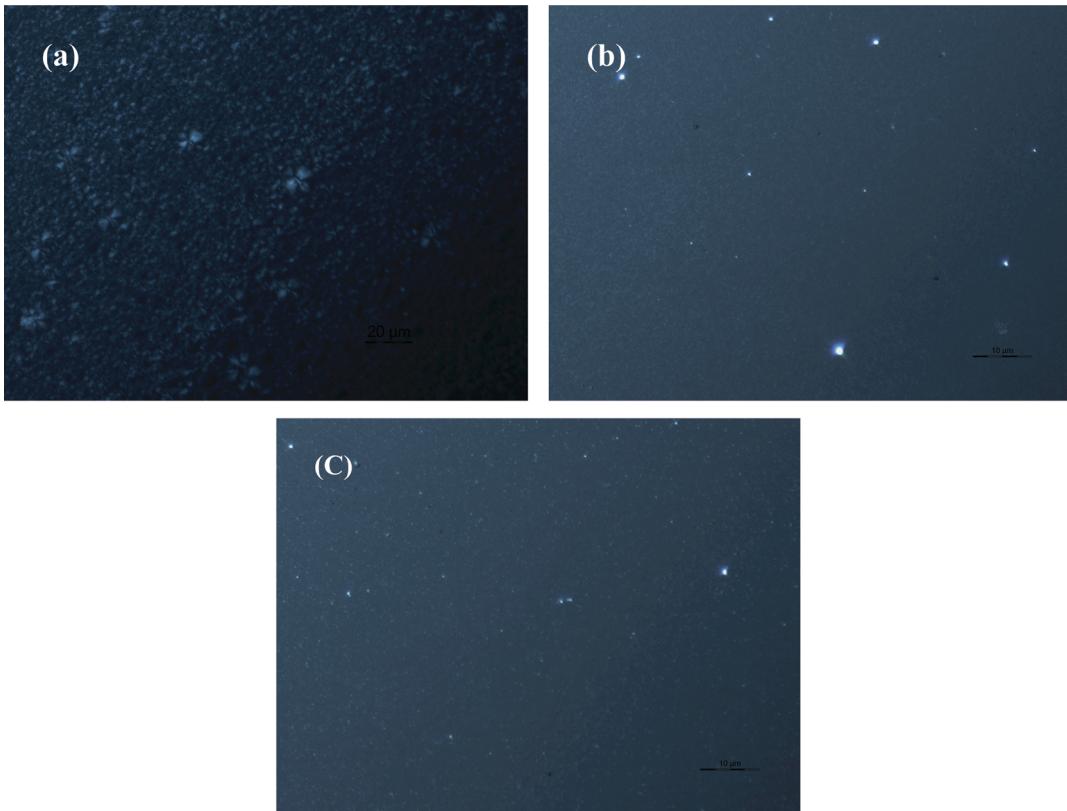
the characteristic morphology of the  $\alpha$ -phase is observed in some portions, corroborating the FTIR data. However, no birefringence pattern is observed in the PNC2.5 and PNC11 samples, which discounts the possibility of formation of the  $\gamma$ -phase which also exhibits a birefringence pattern.<sup>13–15</sup> We therefore are led to believe that the  $\beta$ -phase formation is complete in the newly reported samples.

Moreover, the mechanism of formation of AgNP and that of its composite formation must almost be the same in our experiment and the experiment undertaken by Mandal et al.,<sup>6</sup> as the experimental condition used by the latter does not differ much from that adopted in our work.<sup>1</sup> We have used 1% (w/v) PVDF solution in *N,N*-dimethylformamide (DMF) stirred for 10 days at  $30\text{ }^\circ\text{C}$ , while they have stirred 6% (w/v) PVDF solution in DMF for 12 h at  $60\text{ }^\circ\text{C}$ . At the higher temperature used by Mandal et al., the rate of AgNP formation is higher and Mandal et al. obtained the  $\beta$ -phase. In the method reported by us, the rate of AgNP formation is slower, as the temperature is lower by  $\sim 30\text{ }^\circ\text{C}$ . The slower rate of AgNP formation would eventually convert all the PVDF (as the PVDF concentration is also low) into the  $\beta$ -phase (in the presence of a sufficient amount of AgNP) because the nucleation of  $\beta$ -phase PVDF occurs at the AgNP surface. Since the PVDF concentration is low, the growth

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**Figure 2.** Polarized optical micrograph of the newly prepared Ag/PVDF nanocomposite thin films: (a) PNC 0.5; (b) PNC2.5; (c) PNC11.

rate of  $\beta$ -PVDF is also low, making the crystal more perfect and leading to a melting point higher than that of  $\alpha$ -phase PVDF.

Therefore, the new experimental evidence reported here points to the “formation of piezoelectric polymorph”, supporting the title of the commented article.<sup>1</sup>

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## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: psuakn@mahendra.iacs.res.in.

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