Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Interfacial-Interaction Induced Modifications in Segmental Dynamics and Free Volume of Poly(ethyleneimine) Canopy in Nanoparticle–Organic Hybrid Materials: An Investigation by Temperature Dependent Broadband Dielectric and Positron Annihilation Spectroscopy

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Positron Annihilation Lifetime Spectroscopy

Experimental:

For the PALS measurements, ^{22}Na (10 μCi) sealed in thin Mylar films was used as a positron source. In order to avoid direct sticking of neat PEI or NOHMs to the source, an extra Mylar layer was used to protect the source. This source was fully covered by the sufficient amount of the sample to stop all the emitted positrons within it. The sample and source assembly sealed in a copper sample holder was placed on the cold tip of a cooling system having temperature accuracy of 0.5 K. PALS spectrometer consisting of two fast scintillation BaF_2 detectors were placed perpendicular to each other facing the cold tip to record the birth (1274 keV) and annihilation gamma (511 keV) radiations from the sample. The BaF_2 detectors are connected to a fast-fast coincidence circuit. The time resolution of the spectrometer determined using ^{60}Co radioisotope is 0.240 ns. Source corrections (positron fraction annihilating in the source material and coverings), was estimated using a reference material i.e. silicon single crystal (bulk positron lifetime: 0.220 ns). The estimated source correction components were 0.397 and 1.73 ns with corresponding intensities of 12.0 and 0.8 %, respectively. PALS spectra consisting of ~ 1 million counts were acquired at different temperatures to determine the temperature dependent free volume variations of PEI. All the PALS spectra were analyzed using computer program PALSfit [S1] in discrete positron lifetime components.

Methodology:

PALS measurements are performed by implanting positrons from a sealed radioactive source (^{22}Na) to the sample. The high energy positrons are quickly thermalized through elastic or inelastic interactions within the material. In molecular solids of low density like polymers and porous materials, in addition to annihilation with electrons, formation of a bound state of positron and electron viz. positronium (Ps) occurs. Ps, akin to hydrogen atom, exists in two energy states viz. *para*-positronium or *p*-Ps and *ortho*-positronium or *o*-Ps. These states are formed in 1:3 ratios due to multiplicities of spin orientation of the electron-positron pair. The annihilation rate of Ps depends on the spin orientation of its constituents. Parallel spins of electron and positron in *o*-Ps forbids the emission of two photons in opposite direction and

hence, its intrinsic annihilation rate is slowed down as compared to p-Ps. As a result of its long intrinsic lifetime (142 ns), *o*-Ps is localized in the low density regions like pores or free volume while diffusing through the material. The localized *o*-Ps continuously collided with the wall of the free volume/pore and undergoes annihilation through an additional mode picking up an opposite-spin electron. This mode of annihilation emitting two 511 gamma photon in opposite direction is called *pick-off* annihilation. Various models based on different theories have been developed to correlate the *o*-Ps pick-off lifetime ($\tau_{o\text{-}Ps}$) with the pore or free volume size (R, nm). Among all these modes, Tao–Eldrup model [S2, S3] is widely used (eq. S1).

$$\frac{1}{\tau_{o-Ps}} = 2\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right] \qquad \text{(S1)}$$

where ΔR = 0.166 nm is an empirical constant, and it represents the electron layer thickness on inner surface of the free volumes.

References:

(S1) P. Kirkegaard and M. Eldrup, *Comput. Phys. Commun.* 1984, **35**, 401–409.

(S2) S. J. Tao, *J. Chem. Phys.* 1972, **56**, 5499−5510.

(S3) M. Eldrup, D. Lightbody and J. N. Sherwood, *Chem. Phys.* 1981, **63**, 51−58.

Table S1: The fitting parameters B, T_V and $\log f_\alpha$ ($f_\alpha = 1/2\pi\tau_\alpha$) evaluated from the fitting of $-\log(\tau_\alpha)$ with 1000/T as shown in Figure 6b through solid lines. Same parameters for secondary (β) relaxation are also shown for which fitting is shown in the inset of Figure 6b.

Sample	**Primary (α) relaxation**			**Secondary (β) Relaxation**		
	B (K)	**T_V (K)**	**$\log f_\alpha$**	**B(K)**	**T_V (K)**	**$\log f_\beta$**
Neat PEI	2704.4	139.2	16.8	1113.4	148.6	10.8
NP-NOHM	1484.5	167.7	14.5	305.9	193.0	8.1
NR-NOHM	1054.5	189.5	12.8	300.4	199.3	7.9

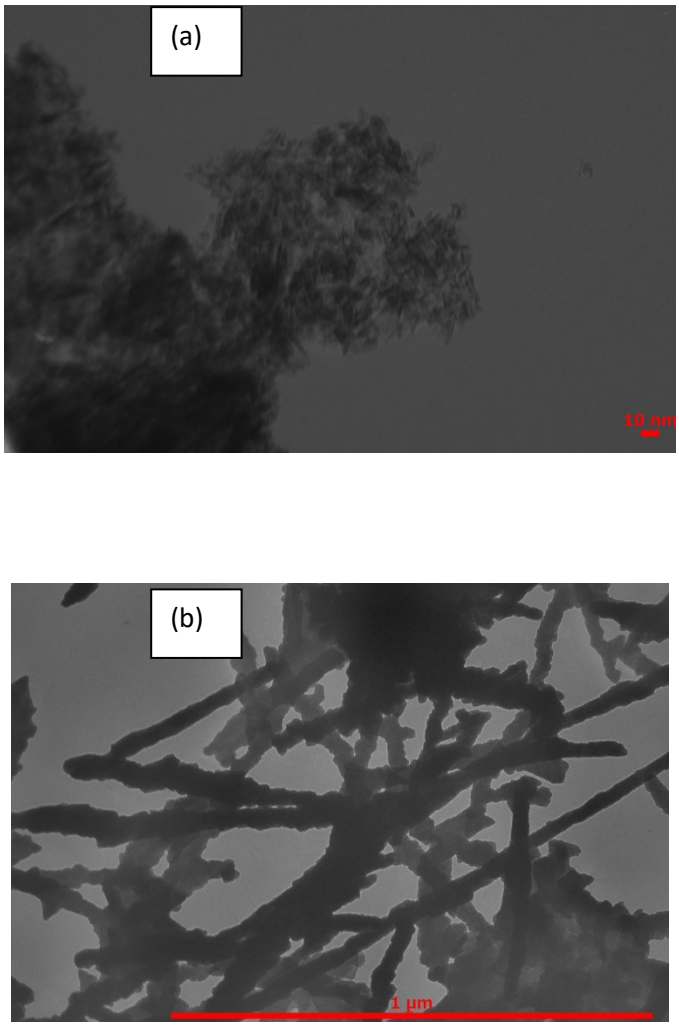


Fig. S1 TEM images of (a) alumina nanoparticles and (b) nanorods.

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC):

TGA (Setsys evolution 1750, SETARAM) and DSC (Mettler Toledo DSC, Switzerland measurements were carried out under N_2 atmosphere at 10 K/ minute heating rate in the temperature range (300 – 900 K) and (180 – 350 K), respectively. The DSC thermograms are shown from the heating cycle which was carried out after a cooling cycle from room temperature to 180 K.

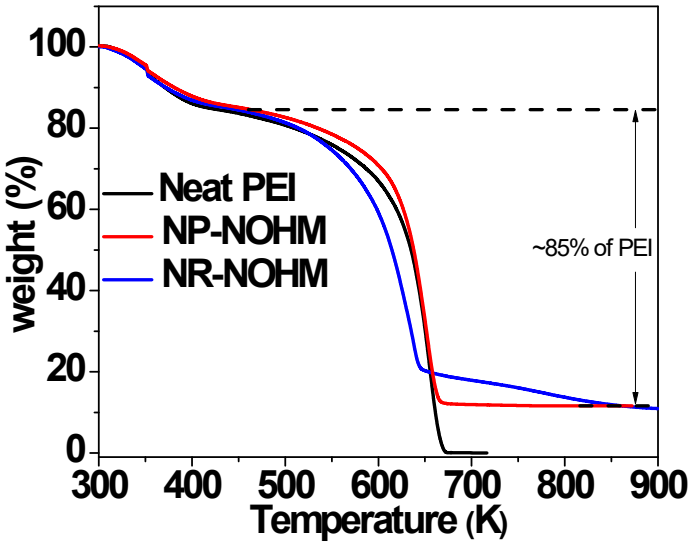


Fig. S2 TGA thermograms of neat PEI, NP–NOHM and NR–NOHMs. Nanocores content (~ 15%) with respect to PEI is calculated as [(wt.% at 850 K)/(wt.% at 450 K - wt.% at 850 K)].

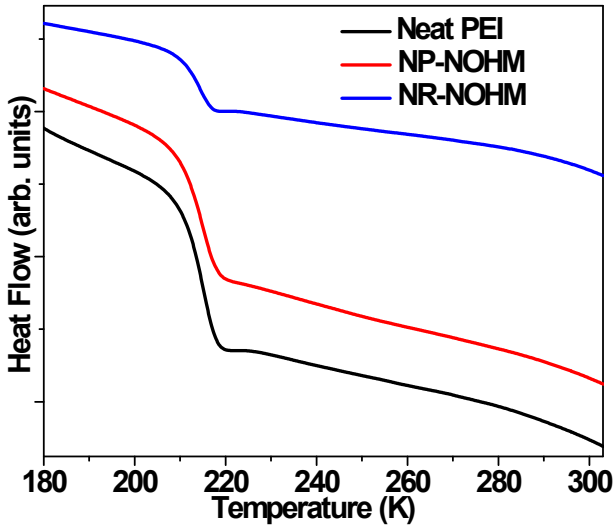


Fig. S3 DSC thermograms of neat PEI, NP–NOHM and NR–NOHMs. The curves have been shifted on the Y axis for the clarity.

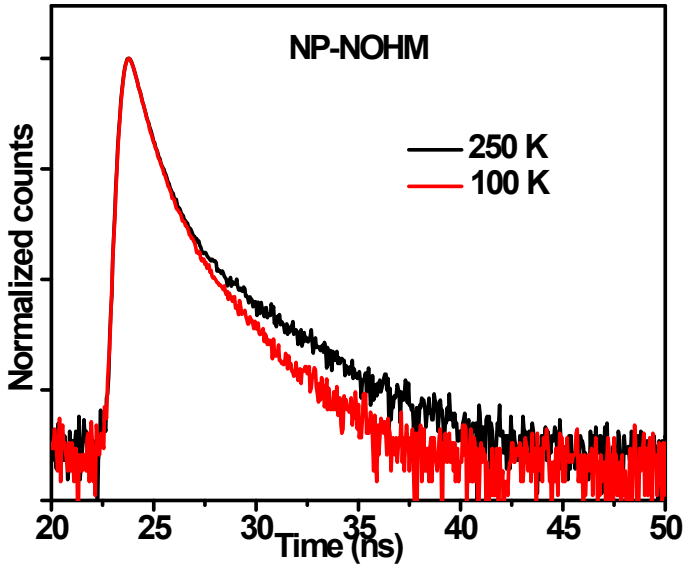
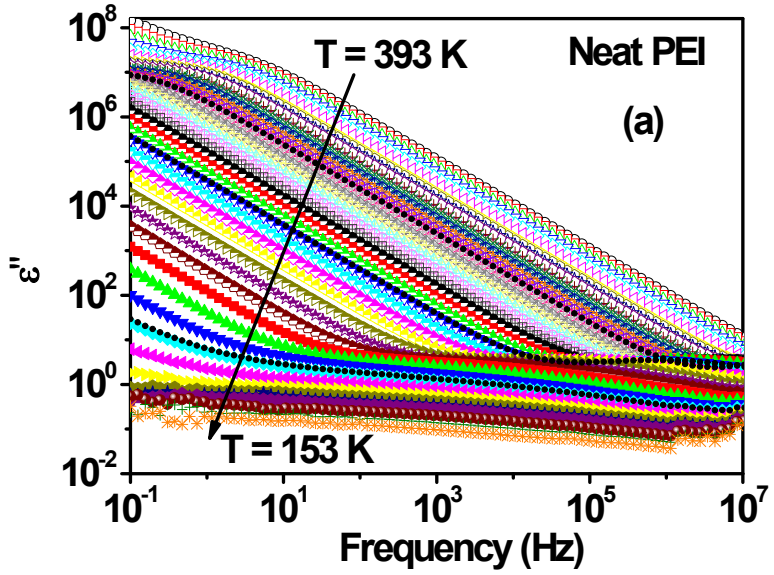
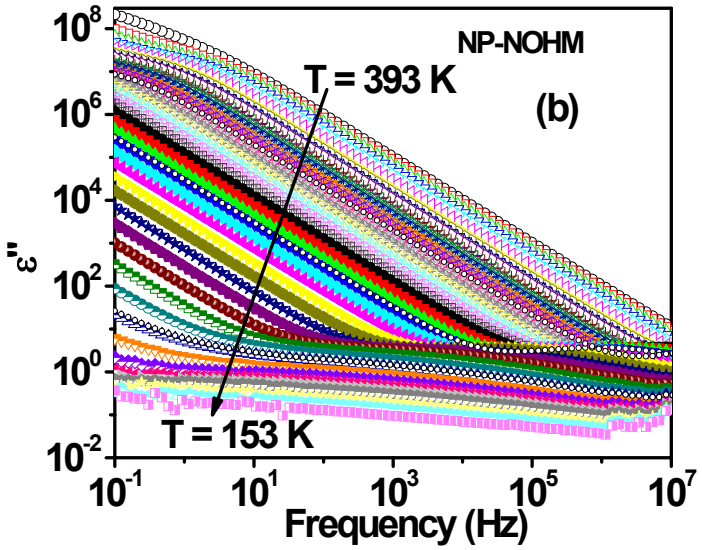


Fig. S4 Typical PALS spectra of NP–NOHM at 100 and 250 K.


Neat PEI
(a)
T = 393 K
T = 153 K
ε''
Frequency (Hz)


NP-NOHM
(b)
T = 393 K
T = 153 K
ε''
Frequency (Hz)

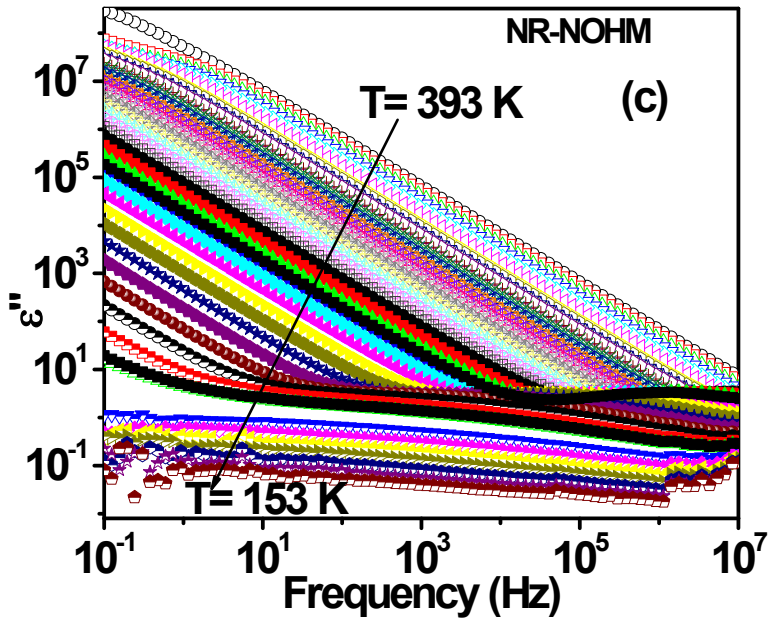


Fig. S5 Frequency dependent dielectric loss parameter (ε'') for the neat PEI and both type of NOHMs in temperature range 153 – 393 K. The filled black data are measured during the heating cycle and confirm the reproducibility. It also confirms that there is no hysteresis during heating and cooling cycle of the measurements.