

Thermal Studies of High Temperature Resistant Phosphorylated Phthalonitrile Resins

Jeetendra Kumar Banshiwal¹, T.U. Patro², A.S. Singh^{1*} and D.S. Bag¹

¹Defence materials and stores research and development establishment (DMSRDE), Kanpur, Uttar Pradesh, India

²Defence Institute of Advanced Technology (DLAT) Pune, Maharashtra, India

*Correspondence to:

A.S. Singh

Defence materials and stores research and development establishment (DMSRDE), Kanpur, Uttar Pradesh, India.

E-mail: acdri2005@gmail.com

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Abstract

Wide processing window-oriented phosphorous containing bis-phthalonitrile resins, bis[3-(3,4-dicyanophenoxy)phenyl] phenyl phosphate (**2c**), and bis[4-(3,4-dicyano phenoxy)phenyl] phenyl phosphate (**2d**) have been prepared by the reaction of monophthalonitrile precursors, 4-(3-hydroxyphenoxy)phthalonitrile (**1c**) and 4-(4-hydroxyphenoxy)phthalonitrile (**1d**) with phenyl phosphoridate dichloride in anhydrous aprotic solvents. The monophthalonitrile precursors were synthesized via nucleophilic substitution reaction of 4-nitrophthalonitrile with resorcinol (**1c**) and hydroquinone (**1d**) respectively in dry polar aprotic solvents preferably in dimethyl sulphoxide (DMSO) at ambient temperature under N₂-atmosphere. The Differential Scanning Calorimetry (DSC) thermogram of uncured resins **2c** and **2d** showed onset of curing at 206 °C and 236 °C, respectively, with a processing window of 181 °C and 136 °C along with a curing window of 120 °C and 131 °C on 10 °C/min heating rate, respectively. The enthalpies of curing reactions for the resins **2c** and **2d** were found to be 33 J/g and 55 J/g, respectively. These resins **2c** and **2d** were then cured in presence of 5 wt% bis[4,4'-bis(3-aminophenoxy)diphenyl] sulphone (m-BAPS) to form corresponding oligomers and further post-curing at the programmed heating schedule to achieve fully cross-linked thermosetting networks, **3c** and **3d**, respectively. The thermogravimetric analysis (TGA) of the fully cured polymers **3c** and **3d** has shown the onset of thermal degradation (T_{ons}) at 389 °C and 404 °C along with char yield of 78 wt% and 79 wt% at 800 °C with 20 °C/min heating rate, respectively, in N₂-atmosphere. The corresponding limiting oxygen index (LOI) values of these cured polymers were found to be 48.7 and 49.1 (calculated by Krevelen's equation). Both the cured polymers **3c** and **3d** have not shown any glass transition temperature (T_g) up to 350 °C (via DSC analysis).

Keywords

Phthalonitrile, Phosphorous, Differential scanning calorimetry, Thermogravimetric analysis, Limiting oxygen index

Introduction

Phthalonitrile (PN) resins are modern day thermosetting polymers which hold outstanding properties [1-7] to be utilized for high temperature applications. These resins system upon curing do not liberate any by-products/ volatiles [8], therefore results void-free and denser cross-linked networks. These resins have an inherent tendency to get cured upon heating tendency but this often lead to decomposition of improper curing, so curatives are being added to initiate curing reactions and hasten the cross-linking process [9]. PN resins having reactive curing functionalities (i.e., self-curing) were reported in literature to initiate the curing reaction thus avoiding addition of external curing additives [10]. PN resins have also been utilized for fabrication of fiber- [11] and fabric-reinforced

composites [12, 13] which have shown much better properties in comparison to composites fabricated with conventional thermosetting resins (i.e., epoxy, phenolic, bismaleimides, polyimides, and cyanate esters). Some of these composites have also been found suitable for naval applications [13, 14] on account of their outstanding flame retardant and low-smoke formation [15] behavior upon burning. The problem associated with PN resins is that they have low-processing and curing windows along with lack of natural tack and poor solubility in common industrial solvents for hand lay-up and pre-impregnation applications. PN resins having above advantageous functionalities, advantageous to thermally stable systems [16]. The present study is focused on developing phosphate ester (well-known as flame retardant) based PN resins which can offer excellent thermo-oxidative stability along with natural tack or low-melting point behavior with wide processing window to ensure proper impregnation of resin in fabric during fabrication of composite through vacuum assisted resin transfer molding [17]. A large-curing window is desired to ensure better cross-linking reaction for high cross-linking density.

Materials and Experimental

Materials

Resorcinol, hydroquinone, dry DMSO, Tetrahydrofuran (THF), iso-propanol, and 4-nitrophthalonitrile chemicals were received from Sigma Aldrich. Anhydrous potassium carbonate (K_2CO_3) was received from Merck. All were used as received without purification. All glass-wares were dried in vacuum oven prior to experiment.

Instrumentation

The 1H -NMR (Nuclear Magnetic Resonance) spectra of prepared resins were recorded by utilizing Bruker Supercon Magnet DRX-400 spectrometer (i.e., 400 MHz operating frequency for 1H -NMR) in DMSO- d_6 solvent. Tetramethylsilane (TMS) (δ .00 ppm) were used as an internal standard in 1H -NMR. Fourier-transform infrared spectra (FT-IR) of synthesized precursors were measured on a FT-IR spectrophotometer (Perkin-Elmer-Model RXI) in range of 400 - 4000 cm^{-1} . DSC was used to measure the melting point (T_m), glass transition temperatures (T_g), and curing temperatures (T_c) of resins and their cured counterparts by TA Instruments, USA with Model No. DSC Q200 with 10 $^{\circ}C/min$ heating rate (β) under N_2 -atmosphere. The degradation temperatures (T_d) for fully cured resins were monitored by TGA on Mettler Toledo scientific instrument of Model No. SDTA 851 with 20 $^{\circ}C/min$ heating rate under inert atmosphere. Water uptake properties of cured resins in form of vacuum dried post-cured films on glass Petri dish, were calculated by the mass difference before and after putting measurement in de-ionized water at ambient temperature for two-days.

Experimental

The resins i.e., **2c** and **2d** were synthesized by the reaction of monophthalonitrile precursors, **1c** and **1d** with phenyl phosphoridate dichloride in anhydrous aprotic solvent THF. Initially, the monophthalonitrile precursors, **1c** and **1d** were prepared through nucleophilic substitution reactions of 4-ni-

trophthalonitrile with resorcinol and hydroquinone respectively in dry polar aprotic solvents (i.e., DMSO) at ambient temperature under N_2 -atmosphere. These resin monomers (**2c** and **2d**) were then cured in presence of 5 wt% 4,4'-bis[4-(3-amino-phenoxy)phenyl] sulphone (m-BAPS) diamine to corresponding thermosetting cross-linked networks i.e., **3c** and **3d**, respectively (Figure 1). The FT-IR spectrograph of **2c** and **2d** resins is shown in figure 2. The curing properties of bis-phthalonitrile resins i.e., **2c** and **2d** and their corresponding polymers **3c** and **3d** were evaluated DSC (Figure 3). The thermal stability of fully cured **3c** and **3d** polymers were measured by TGA (Figure 4).

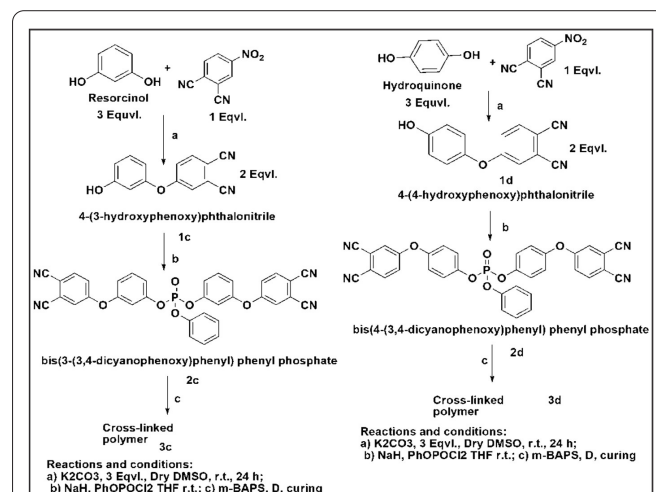


Figure 1: Synthesis of phosphorus substituted bis-phthalonitrile resins **2c** and **2d** and their corresponding polymers **3c** and **3d**.

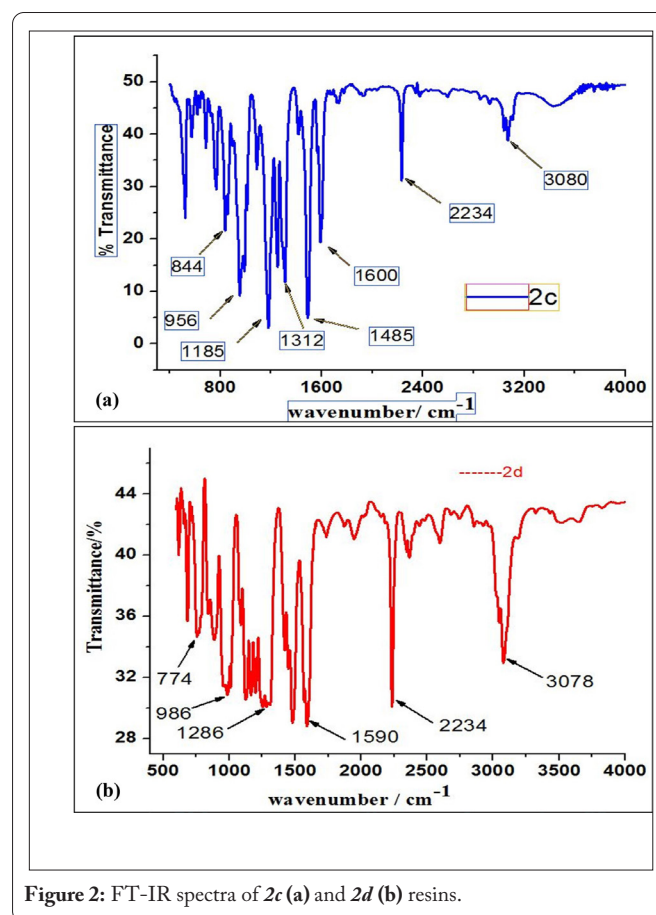


Figure 2: FT-IR spectra of **2c** (a) and **2d** (b) resins.

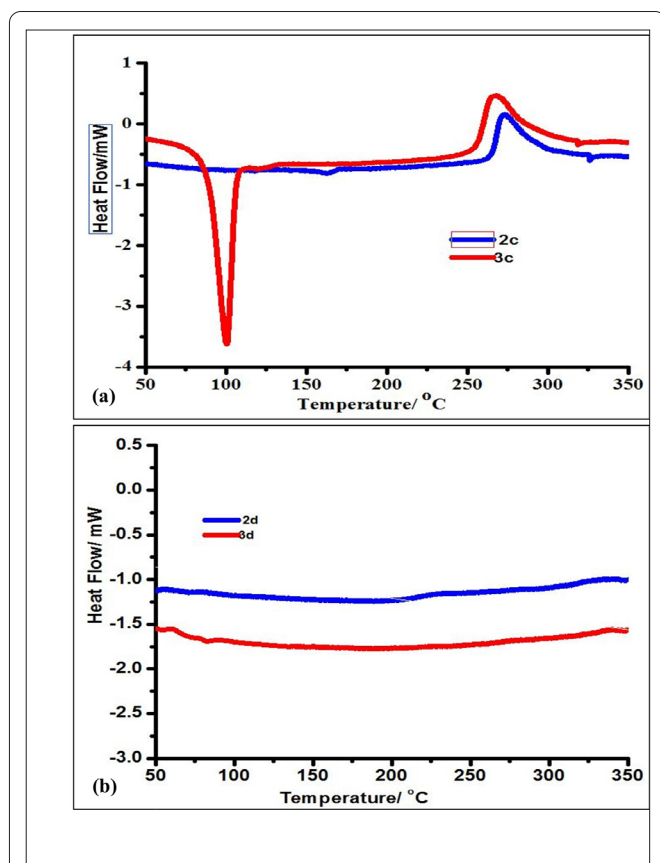


Figure 3: The DSC thermogram; (a) phosphorous containing PN resins (2c and 2d) and (b) their corresponding cured polymers.

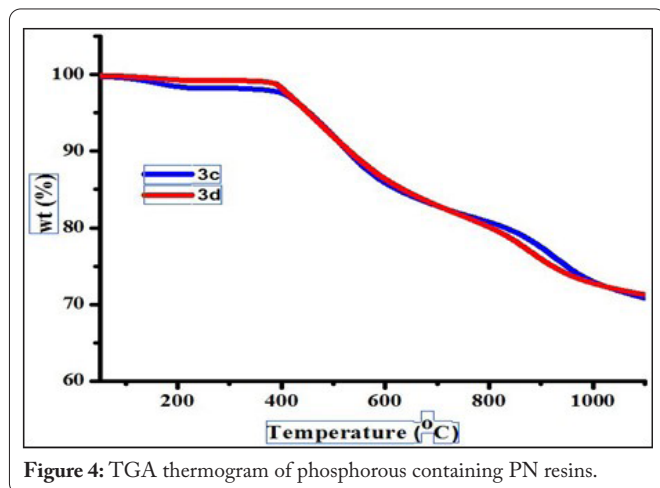


Figure 4: TGA thermogram of phosphorous containing PN resins.

Preparation of phthalonitrile monomers and their respective cross-linked polymer

Synthesis of compound 1c [4-(3-hydroxyphenoxy) phthalonitrile]

Mixture of resorcinol (16.5 g, 150 mmol), 4-nitro phthalonitrile (8.65 g, 50 mmol), and anhydrous K_2CO_3 (13.8 g, 100 mmol) in dry DMSO (250 ml) was stirred for 24 h under N_2 -atmosphere at ambient conditions. Then, to precipitate, the mixture was poured in de-ionized water (2000 ml) and further acidified by gradual addition of HCl (20% solution) till a white precipitate is not found. The precipitate was filtered on sintered funnel and washed with distilled water (3 x 200 ml)

till the precipitate becomes neutral and excess of resorcinol washes out. The precipitate was then washed with 20% solution of isopropanol/water (2 x 100 ml) and further dried at 100 °C /12 h under vacuum oven and obtained pale white powder as compound 1c (20.1, 85.2% yield). Melting Point was found 160 °C (by DSC).

Synthesis of compound 2c [bis[3-(3,4-dicyanophenoxy) phenyl] phenyl phosphate]

To an ice cooled stirred emulsion of NaH (60 wt% in mineral oil) (2.0 g, 40 mmol) in dry THF (100 ml) in inert atmosphere compound 1c (9.4 g, 40 mmol) was added gradually in 30 min followed by stirring for next 2 h at ambient conditions. Phenyl dichlorophosphate (4.22 g, 20 mmol) dissolved in dry THF (20 ml) was then added gradually and added to mixture by using dropping funnel at 0 °C for 20 min and further the mixture was stirred for next 24 h. Then the complete mixture was quenched the next day by drop-wise addition of water, and further extracted with DCM (3 x 200 ml) and dried on rotary evaporator. Column chromatography was used to purify the final products by utilizing silica gel (60 - 120 mesh) with 20% EtOAc/ Hexane as eluant to obtain compound 2c as viscous material (10.40 g, 85.2% yield).

FT-IR (cm^{-1}): 956 (P-O-R stret.), 1409 (P=O stret.), 1590 (C=C-aromatic stret.), 2234 (-CN), and 3080 (-C-H aromatic stret.).

1H -NMR (100 MHz, $CDCl_3$, δ (ppm)): 6.94 (double doublet, 4H), 7.00 (singlet, 2H), 7.18 - 7.28 (m, 9H), 7.36 (tert, 2H), 7.46 (tert, 2H), and 7.74 (d, 2H).

Synthesis of compound 1d [4-(4-hydroxyphenoxy) phthalonitrile]

A mixture of hydroquinone (33.0 g, 300 mmol), 4-nitro phthalonitrile (17.3 g, 100 mmol) and anhydrous K_2CO_3 (27.6 g, 200 mmol) was dissolved in dry DMSO (500 ml) and stirred at ambient conditions in inert-atmosphere for 24 h followed by pouring of resultant solution in de-ionized water (2000 ml) and acidified by gradual addition of 20% HCl solution till a white precipitate cease to form. The precipitate was filtered using sintered funnel and washed with distilled water (3 x 200 ml) till the precipitate becomes neutral and excess of resorcinol washes out. The precipitate was then washed with 20% iso-propanol/water (2 x 100 ml) followed by drying at 100 °C to vacuum to furnish 1d as cream colored powder (19.8 g, 83.9% yield). The melting point was found to be 153 °C (by DSC).

1H -NMR (100 MHz, $CDCl_3$, δ (ppm)): 7.08 (d, 4H), 7.23 (d, 2H), 7.24 (s, 2H), 7.36 (d, 4H), and 7.21 - 7.41 (m, 7H).

Synthesis of compound 2d [bis[4-(3,4-dicyanophenoxy) phenyl] phenyl phosphate]

To an ice cooled stirred emulsion of NaH (60 wt% in mineral oil) (1.0 g, 20 mmol) in dry THF (50 ml) in inert atmosphere compound 1c (4.72 g, 20 mmol) was added gradually for next 15 min followed by stirring at ambient conditions for next 2 h. Phenyl dichlorophosphate (2.11 g, 10 mmol) was added to this mixture via dropping funnel at 0 °C for 10 min followed by stirring for another 24 h. The solution was then

quenched by gradual addition of H₂O with subsequent extraction in DCM (3 x 100 ml). The extract was then dried on rotary evaporator with subsequent column chromatography on silica gel (60 - 120 mesh) with 20% EtOAc/ Hexane to obtain purified compound **2d** as solid of whitish color (5.6 g, 91.8% yield). The melting point was found to be 235 °C (by DSC). The FT-IR spectrum of both resins is shown in figure 2.

FT-IR (cm⁻¹): 986 (P-O-R stret.), 1185 (P=O stret.), 1600 (C=C aromatic str.), 2234 (-C≡N stret.), and 3078 (-C-H stret aromatic).

¹H-NMR (δ ppm): NMR is performed in CDCl₃; 7.08 (d, 4H), 7.23 (d, 2H), 7.24 (s, 2H), 7.36 (d, 4H), and 7.21 - 7.41 (m, 7H).

Preparation of cross-linked polymer 3c and 3d

An amount of m-BAPS (0.025 g, 5% w/w) was mixed with compound **2c** (5 g) followed by initiation of drying cycle in a vacuum oven at 180 °C/2 h, 200 °C/2 h to remove any traces of solvent if present. The resultant dried mixture was then subjected to curing cycle by placing at 250 °C/4 h and 275 °C/4 h then at 300 °C/4 h and 325 °C/6 h and then post cured at 350 °C/6 h and 375 °C/6 h to form thermosetting cross-linked polymeric network (**3c**). The same approach was adopted to synthesize cross-linked polymer (**3d**).

Results and Discussion

Curing process study

The melting and the curing behavior of synthesized resins, **2c** and **2d** and their corresponding thermosets **3c** and **3d** were investigated via DSC under N₂ atmosphere (Figure 3a and 3b and table 2). The DSC scan of **2c** showed onset of curing occurs at 206 °C and observed optimum rate of curing at 273 °C which is completed at 326 °C with wide curing window of 130 °C. The DSC thermogram of cured resin **3c**, absence of any glass transition temperature (*T_g*) up to 350 °C. The DSC thermogram of **2d** showed melting temperature at 100 °C while their curing started at 236 °C and at 265 °C appeared

maximum curing rate which was finished at 367 °C with curing window of 80 °C. The DSC thermogram of its cured counterpart's polymer **3d** has not shown any glass transition temperature (*T_g*) up to 350 °C. The DSC analysis of **2c** and **2d** showed large curing window offer easy processing which can be done without formation of voids. Figure 3 showed all the cured polymers **3c** and **3d** DSC thermogram and showed no glass transition (*T_g*) up to 400 °C which justifies the availability of these resins for fabrication of composites to be utilized for high temperature application (350 ~ 400 °C). Where, *T_m*, *T_{ons}*, *T_{max}*, *T_{end}*, and *T_g* is represented melting point, onset of curing temperature, maximum temperature rate of curing, end-set curing temperature, and glass transition temperature of cured sample, respectively.

Thermogravimetric analysis

The onset degradation temperature (*T_{dons}*) of the resorcinol based phosphorylated polymer resin (**3c**) was found at 389 °C with optimum degradation rate (*T_{dmax}*), and endset temperature (*T_{dend}*), 469 °C and 590 °C, respectively. The char yield was found to be 78% at 800 °C via TGA thermogram. The LOI was found to be 48.7% (experimentally calculated). The TGA of the hydroquinone based phosphorylated polymer resin (**3c**) showed onset degradation (*T_{dons}*), maximum rate of degradation (*T_{dmax}*) and endset (*T_{dend}*) at 404 °C, 521 °C and 594 °C, respectively. The corresponding char yield was found to be 79% at 800 °C. The LOI was found to be 49.1% (calculated experimentally). The TGA analysis of phosphorylated polymers although showed slightly low onset degradation temperature but displayed high char yields and corresponding high LOI values probably due to formation of a protective phosphorylated graphitic layer on polymer surface that prevents further degradation of the polymer. The degradation temperature for cured polymers **3c** and **3d** were measured on TGA under N₂-atmosphere (Figure 4 and table 3). In Table 3, *T_{dons}*, *T_{dmax}*, and *T_{dend}* represent onset degradation, maximum degradation, and final degradation temperature, respectively.

The cured thermoset polymers **3c** and **3d** were also investigated for isothermal ageing by keeping them at 300 °C for 300 h in a heating oven under normal air atmosphere. The isothermal ageing of cured sample phosphorylated phthalonitrile resins **3c** showed 2.85% weight loss while **3d** showed 2.65% weight loss. The LOI calculated through Kreylen's equation by TGA thermogram showed values of 48.7 and 49.1 of **3c** and **3d**, respectively.

[Kreylen's Equation, $LOI=17.5+0.4(\sigma)$ where, σ is referred to wt% char-yield at 800 °C]

Phosphorous containing bis-phthalonitrile resins **2c** and **2d** have been prepared at ambient conditions. The liquid na-

Table 1: The yields of the product are given in varied solvents.

Solvent	% Yield	
	2c	2d
Benzene	60	58
Toluene	64	60
Xylene	66	65
DME	85	88

Table 2: DSC results of synthesized resin monomers, **2c** and **2d** and their respective cured thermosets **3c** and **3d**.

Resins	<i>T_m</i> (°C)	<i>T_{ons}</i> (°C)	<i>T_{dmax}</i> (°C)	<i>T_{dend}</i> (°C)	Processing window	Curing window	<i>T_g</i>
2c	Resin (viscous liquid)	206	273	326	181	120	>350 (3c cured)
2d	100	236	265	367	136	131	>400 (3d cured)

Table 3: TGA analysis of bis-phthalonitrile polymer thermosets **3c** and **3d**.

Product code	<i>T_{dons}</i> (°C)	<i>T_{dmax}</i> (°C)	<i>T_{dend}</i> (°C)	Char yield at 800 °C (%)	Experimental LOI (%)
3c	389	469	590	78	48.7
3d	404	521	594	79	49.1

ture of resin **2c** with viscous behavior provides a natural tack to the resin for fabrication of flexible prepregs. The large processing window of 181 °C and 136 °C of **2c** and **2d**, respectively, offer greater opportunity for fabrication of composites through vacuum assisted resin transfer molding as resin gets enough time for impregnation in the fabric before onset of the curing reaction. A large curing window of 120 °C and 131 °C of **2c** and **2d**, respectively, provide latent curing for high cross-linking density as all the reactive functional group of resins gets sufficient time and opportunity to react and form highly dense cross-linked network, leaving very few un-reactive groups left in cured network. The relatively low onset degradation temperature of **2c** and **2d** is due to oxidation of surface phosphatic groups which form an inorganic phosphate layer along with graphitic layers form due to decomposition of aromatic substituents acts as a barrier which further resist any oxidation leading to high char yield >75% and LOI.

Conclusion

- Phosphorous based resins have been synthesized having penta-valent phosphorous.
- The resins have been characterized by spectroscopic (i.e., FT-IR and ¹H-NMR) and thermal analysis (i.e., TGA and DSC).
- The uncured resin **2c** was found to have natural tack while **2d** was found to be low melting temperature (100 °C).
- Both the resin **2c** and **2d** were found to have large processing window i.e., 181 °C and 136 °C, respectively.
- Both the resins **2c** and **2d** show high char yield of 78% and 79%, respectively, thereby showing flame retardant behavior.
- Both the resins **2c** and **2d** show excellent solubility common industry friendly solvent used in hand lay-up techniques for fabrication of composites

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Conflict of Interest

None.

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