Synthesis and Characterization of Nanocomposites Glyptal Polymer of Titanium, Zirconium and Platinum Metal

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Abstract

Metal-nanocomposites glyptal polymers based on titanium, zirconium and platinum units were synthesized from dehydrated isobutyl alcohol condensed phthalic-anhydrates and glycerol with hydrogen peroxide environment. Metal-nanocomposites reacted with glyptal yields polymeric M–(OBu^i)$_2$ Glyptal is multi-dimensional structures having charge-balancing positive ions and its hydrated in the framework cavities. A statistical study of the effect on the polymerization process of the molar ratio of the component oxides and the water content of the mixture showed the latter to be a critical parameter. The polymerization mechanism and structures of the products were investigated using conductivity, XRD and SEM spectroscopy.

Keywords-*Metal-Nanocomposites, M–(OBu^i)$_2$ Glyptal, Thermostable, Hydrated fluxional.*

Introduction

The strategy for incorporating metal-nanocomposites into polymers and macromolecular systems has often led to new properties and capabilities that would otherwise be challenging for purely-organic analogues to achieve. The increasing research activity in metal-nanocomposites and organometallic polymers is a testament to the opportunity for advancing our fundamental understanding of polymer science and for triggering innovation in various technologies (1,2). Organic polymers have been known for a considerable time, which include monomer units of ethylene n(CH_2-CH_2), polymethylmethacrylate(PMMA), polyvinyl chloride (PVC), ε-Caprolactum, Hexamethylenediamine, adipic acid (3). In general terms a polymer is a compound with a high molecular weight which is made from small repeating units. For instance, in polyvinyl chloride the repeating unit is -CH_2- (CHCl)-. Organic polymers of this type are limited in their applications by their tendency to thermally degrade below 250°C (4,5). To achieve homogeneous dispersions of nanoparticles in polymeric matrices and to enhance the interactions between fillers and polymer matrices during the melt-blending process, several methods are generally applied. The development of science and technology provides the availability of sophisticated products but concurrently increases the use of combustible materials (6). Polymeric materials are commonly used in everyday day life increasing fire hazards and so flame retardants are very often incorporated into them to limit their flammability. This trend can be linked to M–(OBu^i)$_2$ Glyptal the toughening of the legislation in terms of fire hazards combined with the growing use of flame retardants. The flammability behavior of polymers is defined on the basis of several processes and parameters, such as burning rates (solid degradation rate and heat release rate), spread rates (flame, pyrolysis, burn-out, smolder), ignition characteristics (delay time, ignition temperature, critical heat flux for ignition), product distribution (in particular, toxic species emissions), smoke production, etc (7,8). Our goal is then to inhibit or even suppress the combustion process acting chemically and physically in the solid, liquid or gas phase. We can interfere with combustion during a particular stage of this process, e.g.

during heating, decomposition, ignition or flame spread. Three approaches can then be considered to reduce the flammability of polymers (9-11).

In organic synthesis, fire retardants and conducting material industry play a vital role in a growth of our nation; thus, its improvement can help economic growth by increasing the efficiency of organic reagents compounds, polymeric conducting materials and other product. In this research article, nanocomposites metal glyptal polymers, a new class of polymers, having a fundamental role in improvement of polymer, because they have better thermal and conductivity properties and they also act as better organic reagents than the pure glyptal polymer.

Materials and Methods

Materials

Titanium dioxide (TiO_2) molecular weight 79.89g/mol, Zirconiumoxychloride (ZrOCl) m.wt.322.25g/mol, Platinum tetrachloride- ($PtCl_4$) m. wt. 336.896 g/mol, Vanadium pentaoxide (V_2O_5) M. wt.181.88g/mol, Polyvinyl alcohol – $(C_2H_4O)X$,weight average molecular weight 14000 g/mol , Hydrogen peroxide- (H_2O_2) M. wt.34.01 g/mol, Isobutyl alcohol- ($C_4H_{10}O$) M. wt.74.122 g/mol, Phthalic-anhydride –$C_8H_4O_3$ M. wt.142.12g/ml, Toluene- (C_7H_8 , M. wt.92.14 g/mol, Glycerol – $C_3H_8O_3$, M. wt.92.09 g/mol was procured from Thomas Baker (chemicals) pvt. Ltd. Mumbai). All chemical and reagents was research grade.

Synthesis of Nanoparticles

In this research, Synthesis of Organo-metallic Polymer is carried out via the oxidative addition reaction on centre metal atom by approaching the organic monomers in inert condition. In this synthesis, the vacant d orbital's configuration of Ti, Pt & Zr metal atom are used. Synthesis of $Ti(^iOBut)_4$, $Zr(^iOBut)_4$ and $Pt(^iOBut)_4$ from excess amount of iso-butanol. The $Zr(^iOBut)_4$ is obtained by Zirconiumoxychloride (ZrOCl) treating with excess amount of iso-butanol in the presence of Vanadium pentaoxide (V_2O_5) as a promoter catalyst(12). The mixture was refluxed for 5 hours in round bottom flask with water condenser. After refluxing, the mixture was decanted in china dish and dried in hot oven at 80° C. The same procedure was applied for the preparation of $Ti(^iOBut)_4$ and $Pt(^iOBut)_4$ nanoparticles(13,14).

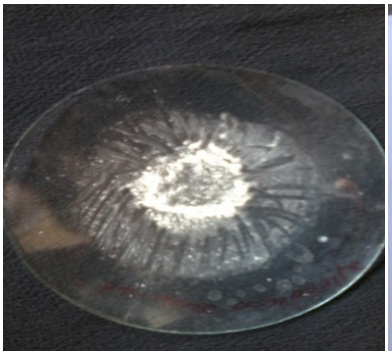

Fig:-01 $Ti(^iOBut)_4$

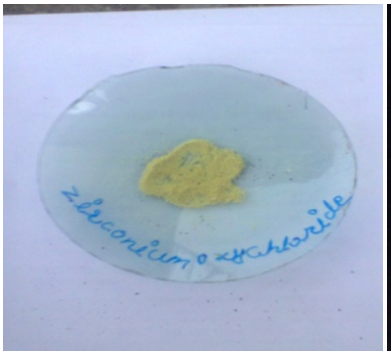

Fig:-02 $Zr(^iOBut)_4$

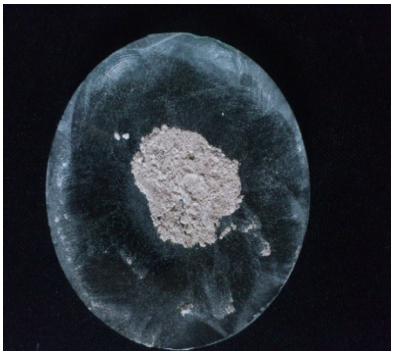

Fig:-03 $Pt(^iOBut)_4$

Synthesis of Nanoparticles Glyptal Polymer

In these syntheses, nanoparticles were fused in glyptal-polymer by condensation polymerization method. Very small amount of $Ti(^iOBut)_4$ nanoparticles are induced in glycerol 0.9209 g/mole treated with phthalic anhydride 1.4212 g/mole. The mixture was first heated vigorously on direct flame in china dish at above 105°C. After well mixing *Ti–$(^iOBut)_2$ Glyptal* polymer was viscous then dried over the sand

bath at 155°C to 165°C. Depending on the ratio of nanoparticles we have synthesized in various proportions of Ti–(^{i}OBut)$_2$ Glyptal polymer. In the same way, we have synthesized other polymers i.e. Zr(^{i}OBut)$_2$ glyptal and Pt(^{i}OBut)$_2$ glyptal respectively.

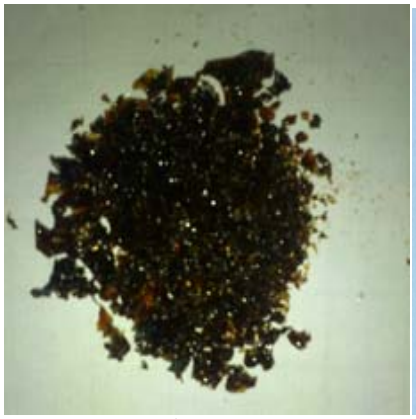

Fig:-04 Ti(^{i}OBut)$_2$Glyptal

Fig:-05 Zr(^{i}OBut)$_2$Glyptal

Fig:-06 Pt(^{i}OBut)$_2$Glyptal

Table 1 Ti(^{i}OBut)$_2$Glyptal

Sr.no.	Ti(^{i}OBut)$_4$	Phthalic-anhydride	Glycerol
1.	0.0303 g	3.52 g	1.4 ml
2.	0.0209 g	3.52 g	1.4 ml
3.	0.0105 g	3.52 g	1.4 ml

Table 2 Zr(^{i}OBut)$_2$Glyptal

Sr.no.	Zr(^{i}OBut)$_4$	Phthalic-anhydride	Glycerol
1.	0.0265g	3.52 g	1.4 ml
2.	0.0182 g	3.52 g	1.4 ml
3.	0.0103 g	3.52 g	1.4 ml

Table 3 Pt(^{i}OBut)$_2$Glyptal

Sr.no.	Ti(^{i}OBut)$_4$	Phthalic-anhydride	Glycerol
1.	0.0043 g	3.7 g	1.6 ml
2.	0.0036 g	3.7 g	1.6 ml
3.	0.0021 g	3.7 g	1.6 ml

Characterization

XRD Analysis Ti(^{i}OBut)$_2$Glyptal

Measurement Date / Time	3/30/2015 3:01:23 PM	Scan Axis	Gonio
Start Position [°2Th.]	10.0142	End Position [°2Th.]	100.0062
Step Size [°2Th.]	0.0080	Scan Step Time [s]	14.5925
Scan Type	Continuous	PSD Mode	Scanning
PSD Length [°2Th.]	2.12	Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed	Divergence Slit Size [°]	0.4785
Specimen Length [mm]	10.00	Measurement Temp.[°C]	25.00
Anode Material	Cu	K-Alpha1 [Å]	1.54060
Goniometer Radius [mm]	240.00	Dist. Focus-Diverg. Slit [mm]	91.00

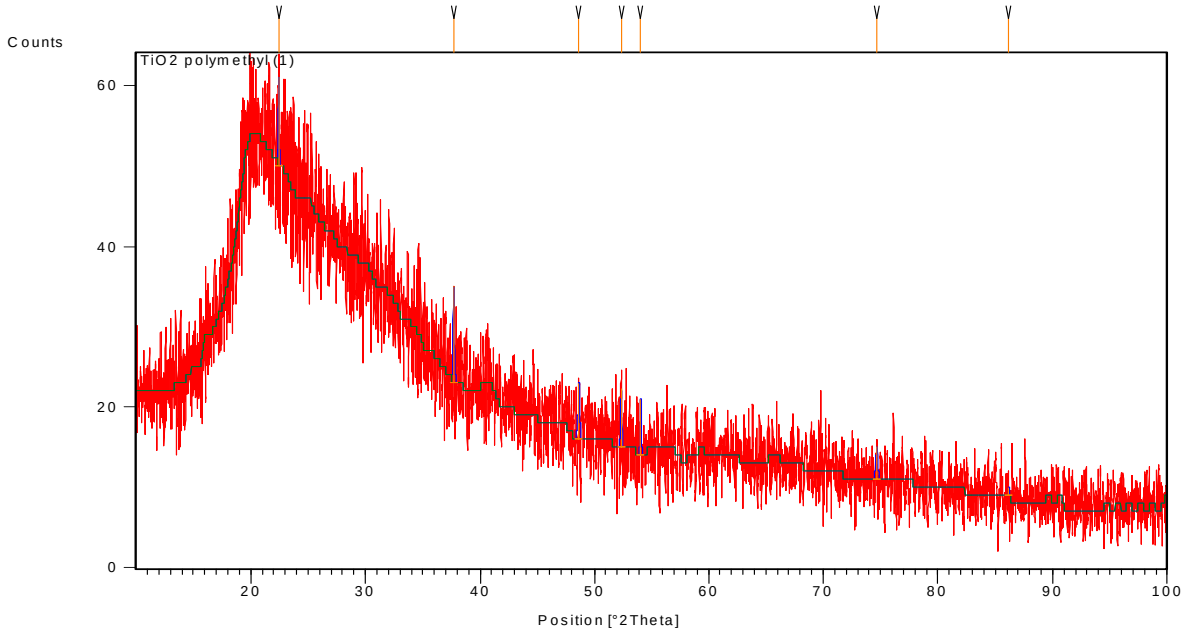

Fig. 07 shows the Ti(^{i}OBut)$_2$Glyptal XRD patterns in the range above 75^{o}.

Calculation of Particle Size from XRD Data

From the XRD data, considering the peak at degrees, average particle size has been estimated by using *Debye-Scherer formula* is D= 0.9 λ / β cos θ. Inter-planar spacing between atoms (d-spacing) is calculated using *Bragg's Law is* 2dsin θ = n λ and enumerated in Table 4.

Where, λ is wave length of X-Ray (0.1540 nm), β is FWHM (full width at half maximum), θ is diffraction angle, d is d-spacing and D is particle diameter size.

Table 4 XRD of Ti(^{i}OBut)$_2$Glyptal polymer

Pos. [°2Th.] (θ)	2 θ	cos θ	sin θ	FWHM [°2Th.] (β)	β cos θ	Size of particles (D)(nm)	d-spacing [Å]	Rel. Int. [%]
25.6105	51.221	0.9017	0.4322	0.4896	0.4414	0.3140	3.47548	100.00
48.1750	96.351	0.6668	0.7451	0.1428	0.0952	1.4558	1.88738	78.21
55.3386	110.67	0.5687	0.8225	0.4080	0.2320	0.5974	1.65881	32.89
62.6162	125.232	0.4599	0.8879	0.9792	0.4503	0.3077	1.48237	23.42
64.9107	129.821	0.4240	0.9056	0.1428	0.0605	2.2901	1.43541	36.18
75.0226	150.045	0.2584	0.9660	0.4896	0.1265	1.0956	1.26503	28.34

XRD Analysis Zr(^{i}OBut)$_2$Glyptal polymer

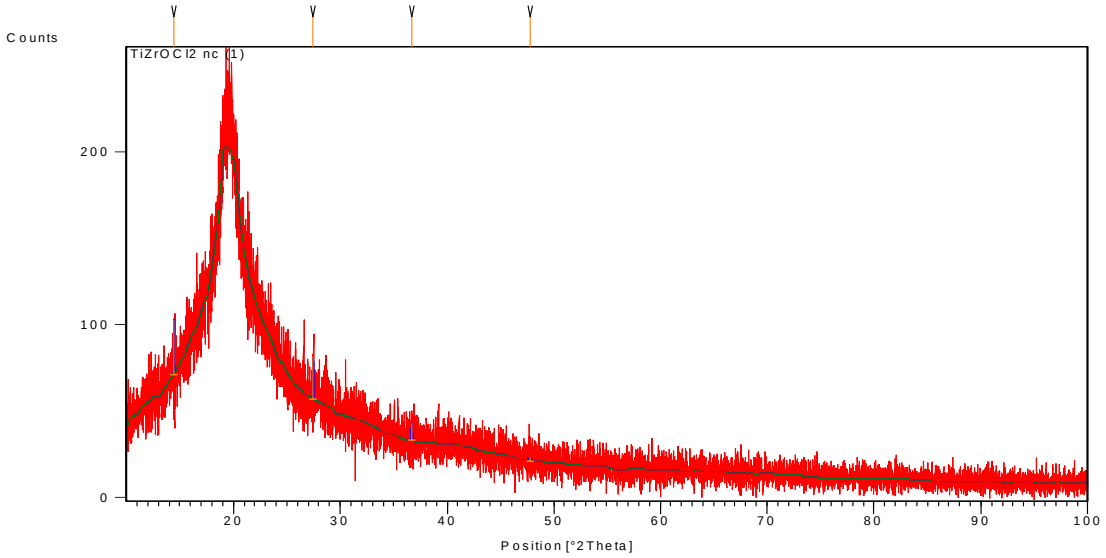

Fig. 08 shows the Zr(^{i}OBut)$_2$Glyptal XRD patterns in the range above 50^{o}.

Calculation of Particle Size from XRD Data

Table 5 XRD of Zr(^{i}OBut)$_2$Glyptal polymer

Pos. [°2Th.] **(θ)**	2 **θ**	Cos **θ**	Sin **θ**	FWHM [°2Th.] (β)	βCos **θ**	Size of particle (D)(nm)	d-spacing [A^{0}]	Rel.int. [%]	height
14.4622	28.9244	0.9683	0.24974	0.0384	0.03718	3.727811	6.11971	100.00	31.72
27.4904	54.9808	0.8870	0.4616	0.0576	0.05109	2.71286	3.24194	76.29	24.20
36.6684	73.3368	0.8021	0.59718	0.1344	0.10780	1.285714	2.44882	30.09	9.54
47.7485	95.497	0.6723	0.74020	0.2688	0.18073	0.76689	1.90324	7.23	2.29

XRD Analysis Pt(^{i}OBut)$_2$Glyptal polymer

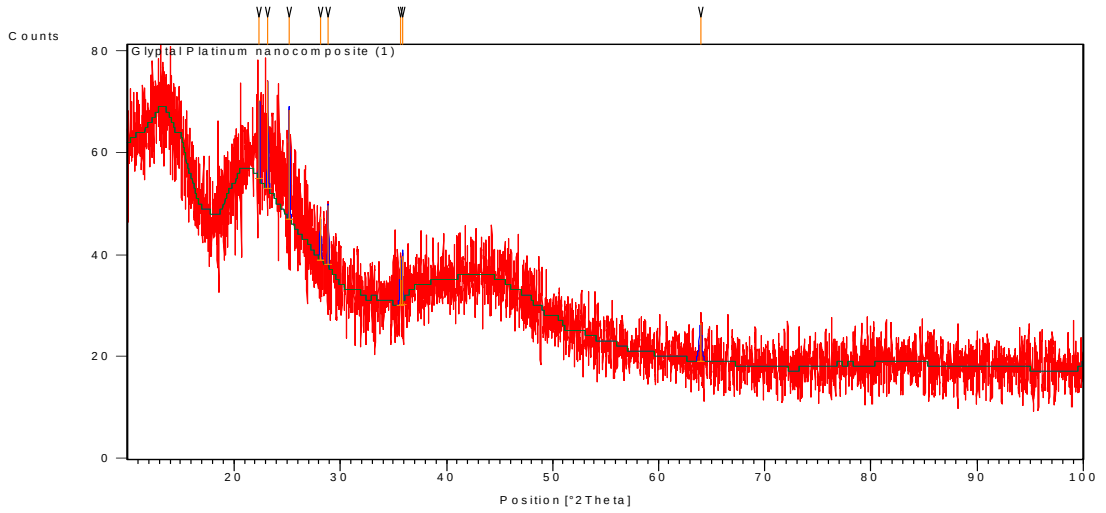

Fig. 9 shows the Pt(^{i}OBut)$_2$Glyptal XRD patterns in the range above 65^{o}.

Calculation of Particle Size from XRD Data

Table 6 XRD of Pt(^{i}OBut)$_2$Glyptal polymer

Pos. [°2Th.] (θ)	2 θ	cos θ	sin θ	FWHM [°2Th.] (β)	β cos θ	Size of particles (D)(nm)	d-spacing [Å]	Rel. Int.[%]	Height [cts]
22.4101	44.8202	0.9244	0.3812	0.0864	0.0798	1.7368	3.96406	71.78	15.37
23.1920	46.384	0.9191	0.3938	0.0672	0.0617	2.2463	3.83215	97.95	20.98
25.2358	50.4716	0.045	0.4263	0.0576	0.0520	2.6653	3.52622	100.00	21.42
28.1466	56.2932	0.8817	0.4717	0.1152	0.1015	1.3655	3.16783	39.00	8.35
28.8799	57.7598	0.8756	0.4829	0.0768	0.0672	2.0625	3.08904	54.74	11.72
35.6827	71.3657	0.8122	0.5832	0.1344	0.1091	1.2707	2.51418	43.89	9.40
35.8393	71.6786	0.8106	0.5855	0.0864	0.0700	1.98	2.50355	44.22	9.47

SEM Analysis for Pt(^{i}OBut)$_2$Glyptal polymer

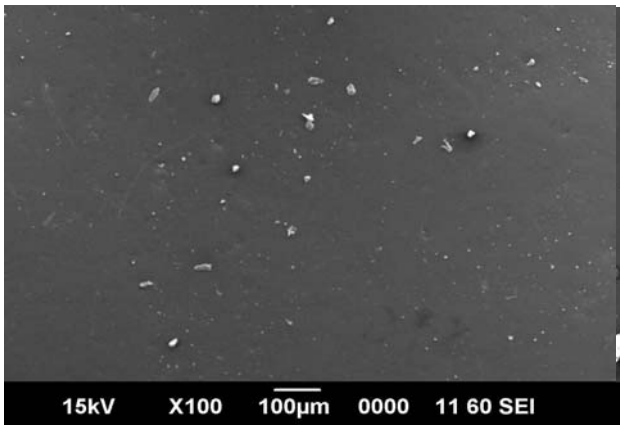

Fig.10

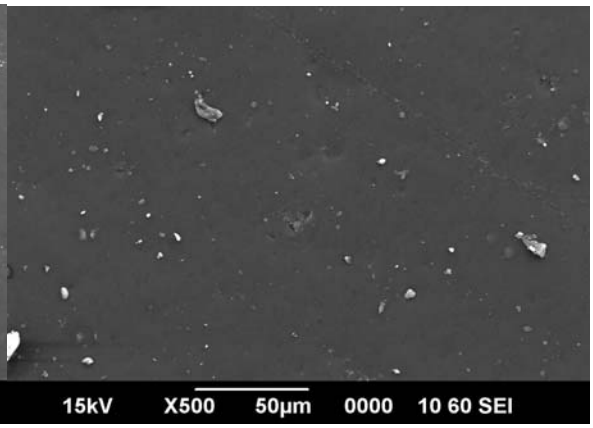

Fig.11

Conductivity, Melting point and solubility of Ti(^{i}OBut)$_2$ glyptal, Zr(^{i}OBut)$_2$ glyptal and Pt(^{i}OBut)$_2$glyptal

Ti(^{i}OBut)$_2$Glyptal polymer almost insoluble in all organic solvent i.e. n-Hexane, Benzene, Toluene and water etc. but partially soluble in dioxane at temperature range 83-88^{o}C. The very small amounts of metal nanoparticles when added to the metal glyptal polymer has been shown the partially conductivity. We have determined the melting point by open capillary method. It is stable at very high temperature and the range are between 165-187^{o}C.

Conclusion

The XRD and SEM analysis ensures the insertion of metal nanoparticles in glyptal polymer. We have successfully synthesized Ti(^{i}OBut)$_2$ glyptal, Zr(^{i}OBut)$_2$ glyptal and Pt(^{i}OBut)$_2$glyptal polymer in a versatile and bio safe approach, at room temperature with using V_2O_5 as a promoter catalyst. A single source catalyst, simple economic and environmentally safe which will make it suitable for various applications in organometallic reagent. Dispersion of nanoparticles between organic polymers improves the thermal stability, organometallic properties and surface phenomenon. XRD analysis have confirmed that synthesized particle are tetragonal anatase phase M(^{i}OBut)$_2$ glyptal and their average nano size is

approximately 0.3174 nm to 3.7278 nm. We expect that this synthesis technique would be extended to prepare many other important metal oxide nano structures.

References

[1] S. Bourbigot, M. Le Bras and J. Troitzsch, Introduction, in Flammability Handbook, ed. J. Troitzsch, Hanser Verlag Pub., Munich, 2003, pp. 3–7.
[2] Fire Statistics, United Kingdom, Office of the Deputy Prime Minister, London, 2004.
[3] Plastics Additives and Compounding, Nov/Dec 2005, p. 8.
[4] M. Le Bras, D. Price and S. Bourbigot, Smoke Development and Suppression, in Flammability Handbook, ed. J. Troitzsch, Hanser Verlag Pub., Munich, 2003, pp. 189–206.
[5] S. Bourbigot and X. Flambard, Fire Mater., 2002, 26, 155.
[6] D. Chen, Y. Z. Wang, X. P. Hu, D. Y. Wang, M. H. Qu and B. Yang, Polym. Degrad. Stab., 2005, 88, 349.
[7] J. Choi, A. F. Yee and R. M. Laine, Macromolecules, 2003, 36(15), 5666.
[8] H. L. Vandersall, J. Fire Flammability, 1971, 2, 97.
[9] S. Bourbigot, S. Duquesne and C. Jama, Macromol. Symp., 2006, 233(1), 180.
[10] V. Babrauskas, Fire Mater., 1984, 8, 81.
[11] Novak, B. M. Hybrid nanocomposite materials—between inorganic glasses and organic polymers. Adv. Mater. 5, 422–433 (1993).
[12] Schubert, U., Husing, N. & Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. Chem. Mater. 7, 2010–2027 (1995).
[13] Wen, J. & Wilkes, G.L. Organic/inorganic hybrid network materials by the sol-gel approach. Chem. Mater. 8, 1667–1681 (1996).
[14] Beecroft, L. L. & Ober, C. K. Nanocomposite materials for optical applications. Chem. Mater. 9, 1302– 1317 (1997)