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Structure and optical properties of $(Alq_x)/Al_2O_3$ ethanol colloids

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An investigation into the structure and chemical stability of green light emitting aluminum complexes of 8-hydroxyquinoline $(Alq_x)/Al_2O_3$ colloids was performed. $(Alq_x)/Al_2O_3$ ethanol colloid was characterized by the high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy, thermogravimetric and simultaneous differential thermal analysis, and thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA/FTIR). The results show that the $(Alq_x)/Al_2O_3$ nanoparticles are composed of an inner core of crystalline Al_2O_3 and an outer layer of 8-hydroxyquinoline (Q) coordinated to the surface aluminum ions of Al_2O_3 the nanoparticles. The luminescence intensity of the $(Alq_x)/Al_2O_3$ ethanol colloids decreased upon the increasing aging time, and is accompanying by the presence of a brown material and a dark brown deposit produced in the colloids. The main component of the deposit was polystyrene. These findings can be explained by a process where Q coordinates to the surface ions of the Al_2O_3 particles, followed by degradation of the pyridine ring of 8-hydroquinonline, leading to the formation of polystyrene.

Keywords: *$(Alq_x)/Al_2O_3$ nanoparticles; ethanol colloids; pulsed laser ablation; optical properties; structure*

1. Introduction

Aluminum complex of 8-hydroxyquinoline (Alq_3) is a stable metal complex that can be sublimed to yield a thin film and stands as one of the most useful materials used in organic light emitting devices for display applications [1–3] and panel displays [1, 4]. Organic-polymeric light emitting diodes (LEDs) exhibit many advantages over inorganic LEDs driven by low dc voltage, high luminous efficiency, high brightness and multicolour emission. Although much progress has been made in improving emission efficiencies and brightness and in prolonging the lifetime of the devices, they still suffer from a limited lifetime due to degradation of Alq_3 molecules [5]. Degradation of luminescence materials in organic light emitting diodes (OLED) is an area of intense

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scientific interest. Baldacchini et al. [6] suggested that accelerated failure of OLEDs at elevated temperatures was attributed to degradation of materials and electrode–organic interfaces, together with morphological change (crystallization) of the organic layers. Papadimitrakopoulos et al. [7–9] have recently published a chemical degradation mechanism for Alq_3, where the presence of moisture and oxygen was found to be detrimental to the production of luminescence quenching by-products. This was attributed to a condensation polymerization of the freed Q (8-hydroxyquinoline), to form a dark, non-emissive residue, whose structure has not yet been fully determined. Determination of this unknown polymer is very important because it might contribute to detail degradation of the Alq_3. Xu and his coworker [10] have systematically investigated the nature of the bright clusters, which can be classified as protrusion and grown grain, in/on the moisture-exposed Alq_3 thin film. The protrusion is most likely to be a hydrated Alq_3 species, whereas, the grown grain is attributed to a crystalline Alq_3 structure.

Our laboratory has recently discovered that alumina 8-hydroxyquinoline complexes $(Alq_x)/Al_2O_3$ nanocolloids prepared by focused pulsed laser ablation at the solid Al_2O_3 target and a flowing ethanol solution of Q can radiate intense green light under ultraviolet radiation. The fluorescence intensity of the $(Alq_x)/Al_2O_3$ nanocolloids decreases with the increase in the aging time in the presence of oxygen and moisture [11]. Because of similar properties and the luminescence mechanism between Alq_3 and the coordinated $(Alq_x)/Al_2O_3$ nanoparticles, studying the degradation of the coordinated $(Alq_x)/Al_2O_3$ nanoparticles may be helpful for understanding the detail degradation of the Alq_3.

In this paper, Fourier transform infrared spectroscopy (FTIR), thermogravimetric and simultaneously differential thermal analysis (TG/SDTA), thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA/FTIR) and high resolution transmission electron microscopy (HRTEM) were used to study the structure and chemical stability of the $(Alq_x)/Al_2O_3$ nanocolloids. Increasing the aging time of colloids resulted in changes in the luminescence colour and produced a brown polymer, accompanied by decrease in the photoluminescence intensity. The results show that polystyrene is formed, and leads to fluorescence quenching when the coordinated $(Alq_x)/Al_2O_3$ nanocolloids have been deposited for five months.

2. Experimental

8-hydroxyquinoline (Q) (Sinopharm Chemical Reagent Co., Ltd, SCRC) in ethanol solution (4.2×10^{-4} M) was used as a flowing liquid over the submerged Al_2O_3 target. The Al_2O_3 (SCRC) target was irradiated by a focused laser beam with 532 nm light from a DCR-3G Nd:YAG laser (Spectra Physics Inc.), operating at 10 Hz, at the fluence of 200 mJ/pulse with a pulse width of 8 ns. The spot size of the laser beam on the surface of the target was about 1 mm, and the flowing liquid was flowing over the target at the speed of about 0.05 cm^3/s. Al_2O_3 was submerged at the depth of 1–2 mm, thus the power density of the pulsed laser beam in the focus spot was approximately as high as 3.18×10^9 W/cm^2. Considering the reflection loss from the focused lens, the actual power density is still higher than 10^8 W/cm^2. The whole preparation process was done in a very pure nitrogen atmosphere.

The light yellow granular deposit can be obtained from the $(Alq_x)/Al_2O_3$ ethanol colloids by centrifugal settling and removing the supernatant liquid. The obtained deposit was washed with ethanol (repeated eight times), dried in vacuum, and finally a light yellow powder was obtained and used for characterization by FTIR and TG/SDTA. After aging of $(Alq_x)/Al_2O_3$ ethanol colloids for five months, a deposit material with brown colour can be found at the bottom and inner wall of the vessel. The deposit (ca. 6mg) was used for TG-FTIR characterization.

The HRTEM photographs and selected area electron diffraction (SEAD) were obtained on the FEI F20 transmission electron microscope (Philips Company). Electron micrographs were recorded using 2 drops of $(Alq_x)/Al_2O_3$ nanocolloid solution, applied onto a copper mesh coated with an amorphous carbon film. FTIR was performed on an Avata 360 FT-IR spectrometer. TG/FTIR measurements were recorded with a Mettler Toledo TGA/SDTA 851^e and Nicolet 5700 FT-IR. TG measurements were performed at a 10 °C/min scanning rate, employing a 50 cm^3/min flow of dry nitrogen as a purge gas for the sample and reference cells.

3. Results and discussion

3.1. Structure of the nano Al_2O_3 particles

Figure 1 shows the HRTEM image of the $(Alq_x)/Al_2O_3$ clusters after being prepared for 1 h. It can be seen from Fig. 1a that the aggregated nanoparticles consist of many smaller, irregular 5–10 nm particles. It was previously shown that, over time, the particles produced by pulsed laser ablation grew in size while undergoing a change in shape, from irregular spherical forms [11]. The size of the particles in Fig. 1c is about 5 nm and it is obvious that the nanoparticles are enwrapped by an amorphous layer, because of the absence of sharp edges. The amorphous material is mostly composed of Q or Q on the surface of $(Alq_x)/Al_2O_3$ clusters. Crystal lines are visible in the enwrapped area of Fig. 1d and the calculated interplanar spacing is 0.3421 nm, which corresponds with the (110) (Fig. 1e) diffraction planes, revealing that the $(Alq_x)/Al_2O_3$ clusters consist of Al_2O_3 crystals. From Figure 1b, it is found that the SEAD pattern of the coordinated Al_2O_3 cluster has a distinctive diffraction pattern with many diffraction points. These findings show that the coordinated Al_2O_3 clusters consist of many smaller Al_2O_3 crystals of disordered arrangement. The interplanar spacing and diffracting planes, together with that of JCPDS card are listed in Table 1. It was found that the *d* spacing is similar for the Al_2O_3 and the $(Alq_x)/Al_2O_3$ clusters, and that the $(Alq_x)/Al_2O_3$ clusters have slightly higher *d* spacing. This also indicates that the original particles, produced by pulsed laser ablation of the Al_2O_3 target immersed into flowing liquid, are Al_2O_3 crystals with the size of 5–10 nm. Original particles are coordinated by Q in the liquid, and very soon they congregate and form larger particles.

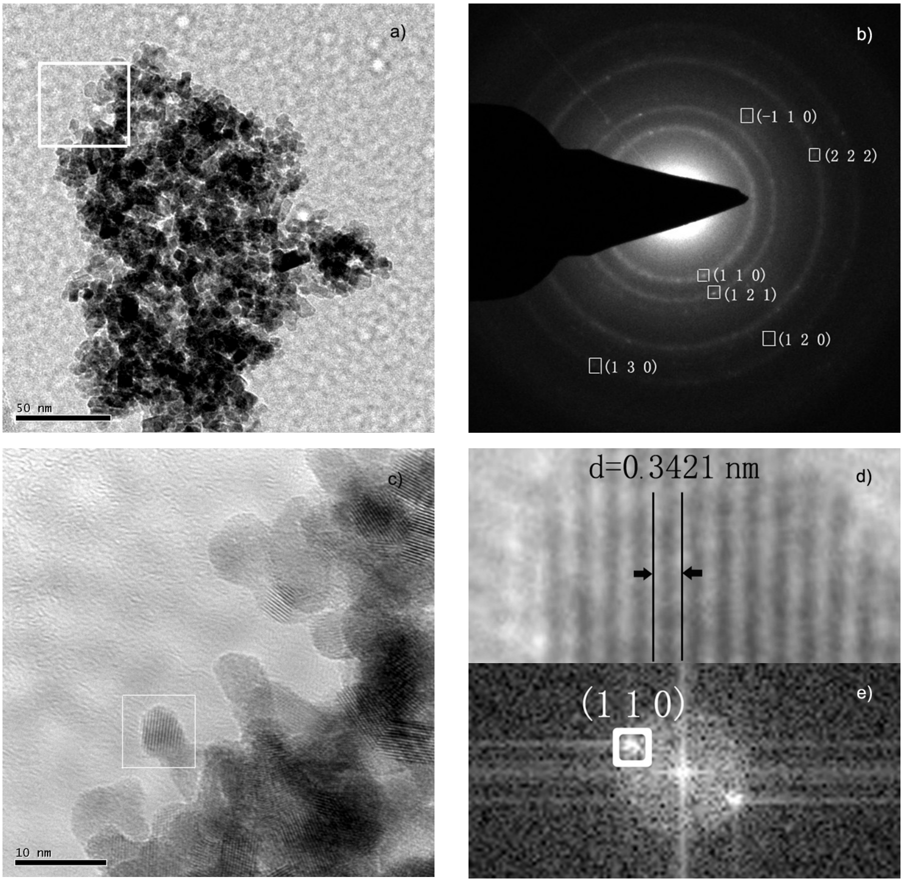

Fig. 1. HRTEM images of the $(Alq_x)/Al_2O_3$ clusters (a), and selected areas (b) of electron diffraction (SAED) patterns of (a), enlarged images (c) and (d) corresponding to the areas marked by the solid line in (a) and (c), and (e) is FFT image of (d)

Table 1. The interplanar spacing and diffraction planes together with that of the JCPDS card

Diffracting planes	Interplanar spacing [nm]	
	Al_2O_3 (JCPDS card 76-0144)	Alq_x/Al_2O_3 cluster
(110)	0.34804	0.3835
(121)	0.25515	0.2976
$(\bar{1}10)$	0.23794	0.2649
(222)	0.21660	0.2281
(120)	0.20855	0.2171
(130)	0.14046	0.1593

Figure 2 shows the FTIR spectra of (Alq$_x$)/Al$_2$O$_3$ clusters and Q from the Aldrich FTIR library. As compared with the spectra of Q and Alq$_3$ reported in the literature [12], the (Alq$_x$)/Al$_2$O$_3$ cluster has much weaker absorbance peaks at about 2920 cm^{-1} (–CH$_2$), 1200–1400 cm^{-1} (quinoline group) and 1580 cm^{-1} (–OH), but has two stronger peaks at 561 and 841 cm^{-1}, which can be attributed to the asymmetric vibrations of Al$_2$O$_3$. It is obvious that the (Alq$_x$)/Al$_2$O$_3$ clusters consist of Al$_2$O$_3$ and Q.

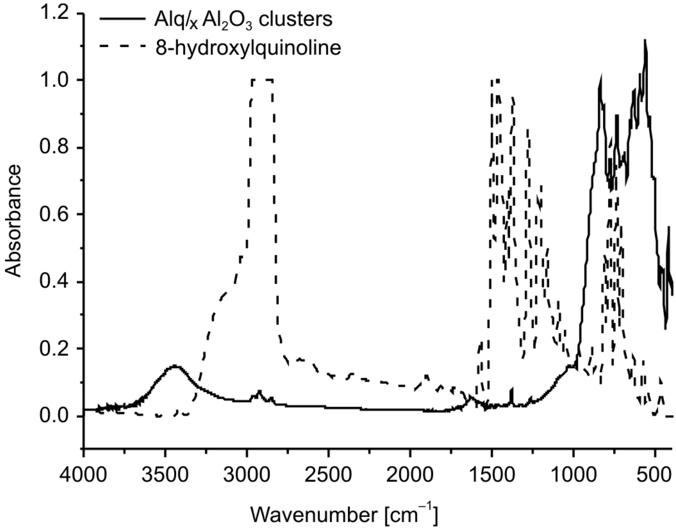

Fig. 2. FTIR spectra of the (Alq$_x$)/Al$_2$O$_3$ clusters and Q from the library of the Aldrich condensed phases

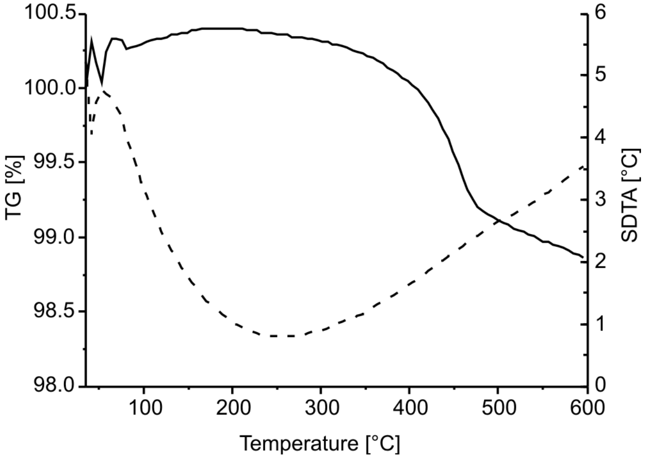

Fig. 3. TG/SDTA image of the (Alq$_x$)/Al$_2$O$_3$ clusters

Figure 3 shows the TG-SDTA image of the (Alq$_x$)/Al$_2$O$_3$ clusters. Above 200 °C (Alq$_x$)/Al$_2$O$_3$ clusters show obvious weight loss (ca. 1.5%) in the temperature range over which the TG-SDTA measurements were conducted. $(Alq_x)/Al_2O_3$ clusters have large surface areas, thus they adsorb much gases (about 0.4%) at temperatures below 200 °C, released at higher temperatures. Thus the weight loss originates from the absorbed gas (about 0.4%) and the thermolysis of Q coordinated to the surface ions of the $(Alq_x)/Al_2O_3$ clusters or simply from its sublimation [8] (1.1%).

3.2. Optical properties of the $(Alq_x)/Al_2O_3$ ethanol colloids

The $(Alq_x)/Al_2O_3$ ethanol colloids can emit strong green fluorescent light under UV irradiation; however, the fluorescence colour changed upon the increasing aging time.

Table 2. The colour of the $(Alq_x)/Al_2O_3$ ethanol colloids with the various aging times under strong white light and UV irradiations

Aging time	The colour under strong white light	The colour under UV radiations
1 h	white	green
1 month	white	light Kelly green
2 months	light brown	Kelly green
5 months	brown	black

Table 2 shows the colour of the $(Alq_x)/Al_2O_3$ ethanol colloids corresponding to various aging times under strong white light and UV irradiations. Under irradiation, differing in time, $(Alq_x)/Al_2O_3$ ethanol colloids display various colours. These findings indicate with the increase in the aging time, a brown, non-fluorescent material is produced in the colloids, and the luminescence intensity decreases. After five months of aging, a deposit material with brown colour can be found at the bottom and inner walls of the vessel. Because the coordinated Znq_2/ZnO ethanol colloids prepared by the same method have very stable chemical properties, and have the same fluorescent green colour during aging [13], alumina was believed to be related to the fluorescence quenching of the coordinated Alq_x/Al_2O_3 colloids. The subsection immediately below describes how FTIR and TG-FTIR were used to characterize the brown deposit material.

Figure 4 shows the FTIR spectra of the deposits of the $(Alq_x)/Al_2O_3$ ethanol colloids and polystyrene (M. W. 50000) from the Aldrich FTIR library. Using pattern-matching software (Omnic 7.2, Thermo Electron corporation), the match value of these two spectra is as high as 95.5%, which shows that the main component of the deposit is polystyrene. In addition, the stronger absorption peak at 3400 cm^{-1} can be attributed to the hydroxyl group, which indicates there is little amount of material containing hydroxyl, which may be the result of Q being absorbed by the deposit.

Figure 5 shows the TG/SDTA image of the deposits of the $(Alq_x)/Al_2O_3$ clusters, and Figure 6 shows FTIR spectra of the thermal products released at 1.1 min, 8.6 min, 41.4 min and also styrene from the flavours and fragrances FTIR library. Weight losses indicating the release of some materials occurred at 1.1, 8.6 and 41.4 min.

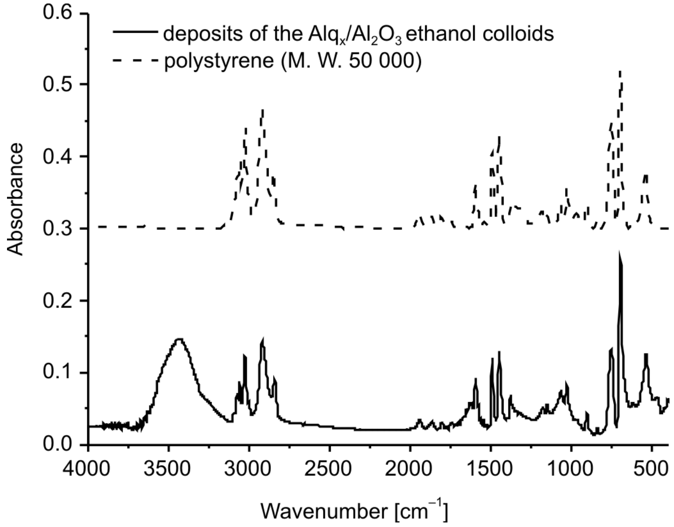

Fig. 4. FTIR spectra of the deposit of the Alq_x/Al_2O_3 ethanol colloids and polystyrene (M. W. 50000) from the Aldrich Condensed Phase Supplement

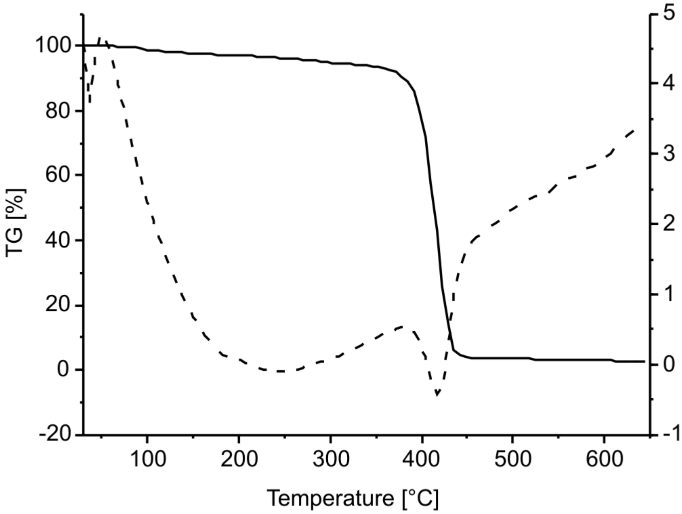

Fig. 5. TG/SDTA image of the deposits of the $(Alq_x)/Al_2O_3$ ethanol colloids

Table 3 shows the weight loss for an $(Alq_x)/Al_2O_3$ cluster in function of time and temperature. The materials released were identified by comparing their spectra with FT-IR spectra from the Aldrich FTIR library. As can be seen from Table 3, a close match of the product released after 41.4 min with styrene indicates these two materials are the same. The small quantity of water was probably absorbed during formation of the colloidal deposits, and ethanol would be expected to absorb into the colloidal deposits as well. As can be seen from Fig. 6 and Table 3, styrene was released in the temperature range of 350–450 °C. It most likely originates from Q coordinated to the surface of the Al_2O_3 particles and also from Q in the colloids.

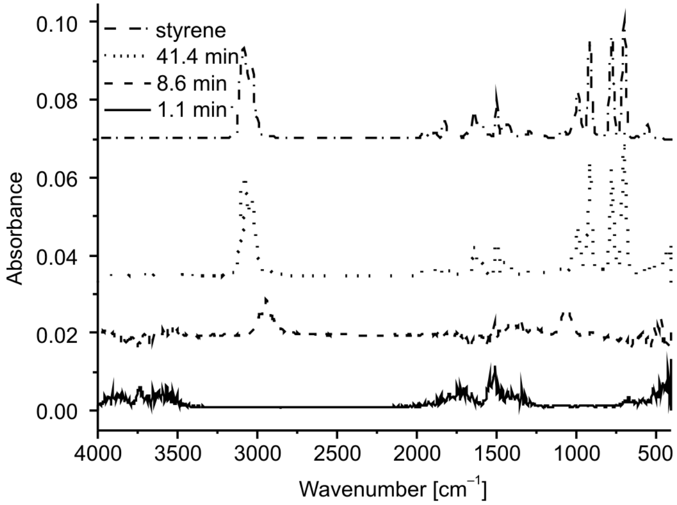

Fig. 6. FTIR spectra of the released thermal products from the deposit at 1.1 min, 8.6 min, 41.4 min and styrene spectrum from the library of flavours and fragrances

Table 3. Weight loss for $(Alq_x)/Al_2O_3$ clusters as a function of time and temperature

Heating time [min]	Temperature [°C]	Weight loss [%]	Rest weight [%]	Match value [%]	Possible released product
1.1	46	–0.34	100.34	45%	water without CO_2
8.6	121	1.7	98.3	60%	ethanol and water
41.4	449	96.29	3.71	96.1	styrene
61.5	650	97.33	2.67		

3.3. Process of decreasing luminescence of the $(Alq_x)/Al_2O_3$ ethanol colloids

It has been shown that $(Alq_x)/Al_2O_3$ nanoparticles are composed of the Al_2O_3 crystal core and Q coordinated with the surface ions of the Al_2O_3 nanoparticles. The luminescence intensity decreases with the increase in the aging time accompanied by the production of a brown material and a dark brown deposit in the colloids. The main component of the deposit is polystyrene. These findings can be explained if Q, coordinated to the surface of Al_2O_3 particles, was catalysed by Al_2O_3 nanoparticles having high surface areas, to form polystyrene. As Q coordinates to the surface Al ions of nanoparticles, some inner bonding energy becomes weaker, some bonds are broken and new ones are formed. The high surface energy of nano Al_2O_3 particles accelerates this change. During the bond changing process, polystyrene and a brown material are formed and Alq_x vanishes. Because this brown material is still unknown, further investigations are presently underway to elucidate the details of luminescence attenuation in $(Alq_x)/Al_2O_3$ ethanol colloids.

4. Conclusions

An investigation into the structure and chemical stability of ethanol colloids of aluminum 8-hydroxyquinoline complexes $(Alq_x)/Al_2O_3$ emitting green light under ultraviolet radiation was performed. The $(Alq_x)/Al_2O_3$ ethanol colloid product was characterized by HRTEM, FTIR, TG/SDTA, TGA/FTIR. The HRTEM and FTIR results showed that crystalline Al_2O_3 is the core of the $(Alq_x)/Al_2O_3$ nanoparticles, with Q coordinated to the surface of aluminum ions of the Al_2O_3 nanoparticles. $(Alq_x)/Al_2O_3$ ethanol colloids with different aging times show different luminescence colours under ultraviolet radiation. The luminescence intensity decreases as the aging time increases, accompanied by the formation of a brown material and a dark brown deposit. TG-FTIR and FTIR results show that the main component of the deposit is polystyrene. These findings can be explained by a process in which Q coordinated to the surface ions of Al_2O_3 particles, is catalysed by Al_2O_3 nanoparticles to form polystyrene.

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