Formaldehyde polymers in interstellar space[1,2]

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[1]Based on an original Cardiff Blue Preprint, published on December 6, 1974 in *Nature*, Vol. 252, 462-463
[2]First discussion of organic polymers in an astronomical context

The precise composition of interstellar dust is as yet unknown. Recent studies of the wavelength dependence of extinction and polarisation favour a composite model of three components : (1) elongated dielectric particles of radii ~10^{-5} cm, which would explain the data in the 1- 0.3μm spectral region; (2) almost spherical graphite particles of radii $\leq 2 \times 10^{-6}$ cm which would explain the near and middle ultraviolet data in $0.3 \geq \lambda \geq 0.2$ μm; and (3) small dielectric particles which contribute mainly to extinction and albedo at wavelengths, $\lambda \leq 0.2$ μm.

There is considerable evidence to support the view that silicate grains exist in circumstellar envelopes around certain cool stars[1]. An emission feature in the 8-12 μm waveband occurring in the spectra of many cool Mira-type stars has been identified with particles of a mineral-like composition. It is also widely believed that silicate dust is responsible for a major part of the observed interstellar extinction and polarization at visual wavelengths, in other words, that silicates make up component (1) above. The evidence for this is not convincing and several strong counter indications already exist. Applications of the Kramers-Kronig relationship to the observed interstellar extinction curve suggest that greater relative abundances of Mg, Si, to H than are consistent with cosmic abundance ratios are necessary to explain the observed extinction[2,3]. This discrepancy could be as much as a factor 10. It seems therefore that the only elements present in sufficient quantity in the interstellar medium to contribute to the observed visual extinction coefficient, $\kappa_V \sim 2$ mag kpc^{-1}, are C,O and N. The possibility of O in the form of H_2O ice has been discussed for many years, although a 3.1 μm ice band was not detected in the spectra of several moderately reddened stars[4,5].

I have argued (N.C.W., unpublished) that formaldehyde molecules which have been detected in over a hundred interstellar clouds could condense on silicate grains. Condensation of H_2CO on silicate grains with temperatures ≤ 20 K is attended by polymerisation into chains

$$CH_2 - O - CH_2 - O \ldots\ldots$$

resulting in the formation if a crystalline polymer known as polyoxymethylene (POM). The constituent elements of this material are sufficiently abundant to provide the main contribution to the mass density of interstellar dust. These particles would grow as long whiskers under interstellar conditions and possess the required dielectric properties to account for component (1) in the composite grain model. In common with many other polymers, POM is moderately refractory with a melting temperature in the range 450 - 500 K. Such grains could survive in HII regions and radiate at temperatures $T_g \leq 500$ K, thus accounting for many galactic infrared sources.

The optical refractive index of epoxy formaldehyde resin, which is likely to be similar to that of POM, is $n = 1.58$ (ref.6). A cylindrical particle of radius close to 1.5×10^{-5} cm, with this value of n, possesses extinction and polarization properties which are consistent with interstellar data[7].

The strongest evidence adduced in support of the view that silicate grains are mainly responsible for the general interstellar extinction is the appearance of an 8-12μm emission feature in the infrared spectrum of the Trapezium nebula, as well as a similar extinction feature in the spectrum of the BN star in the Orion nebula[1,8,9]. Most other 10 μm features observed in stars are confined strictly to circumstellar grains and do not necessarily relate to the behavior of interstellar grains.

By a remarkable coincidence, POM polymers also exhibit strong optical activity in the 8-12μm waveband. Figure 1 shows the absorption spectrum of POM films studied by Tadokoro *et al* [10] for polarized light. Although this feature is comprised of two main bands, as in the case of silicates, a distribution function in the average chain length will mask much of the fine structure, as the precise positions of individual bands depend on this parameter in the crystalline powder.

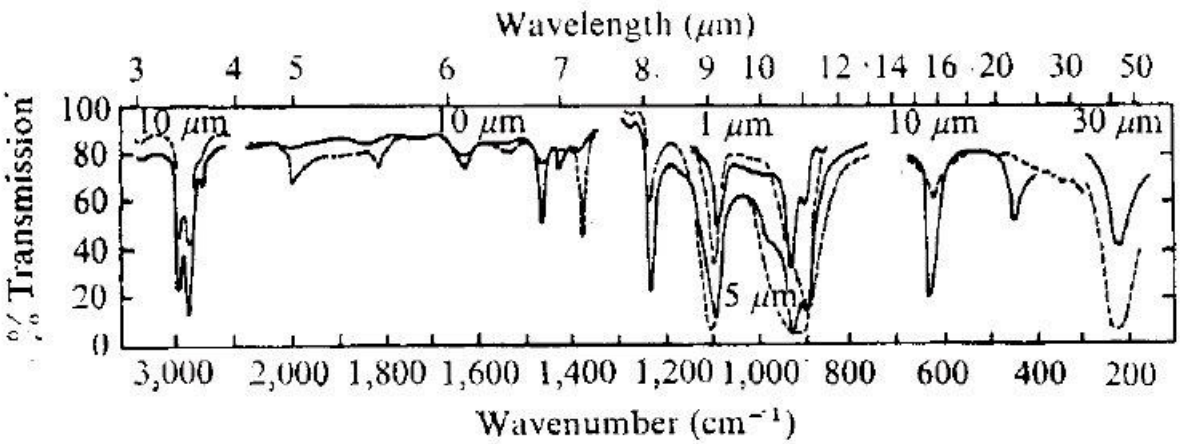

Fig. 1 Infrared transmission spectra for polarized light of POM-films of several thicknesses (1,5,10 and 30μm) for the various wavelength intervals as indicated in the insets. The solid curve refers to light with electric vector perpendicular to crystal axes; dashed curves for electric vector parallel to the crystal axes. (Differing thicknesses of film, 1,5,10 and 30μm, are used over various wavelength intervals. When this is noted, the 8-12μm bands are considerably stronger than others indicated in these data.)

The average mass extinction coefficient at the centre of this band, estimated from the data of Todokoro *et al*[10], is

$$\kappa_{10\ \mu m} \sim 1.4 \times 10^{3}\ cm^{2}g^{-1} \qquad (1)$$

assuming a specific gravity $s = 1.4$ for POM. At the visual wavelength, $\lambda_v = 5{,}470$A, the mass extinction coefficient for POM grains of radii, $a = 1.5 \times 10^{-5}$ cm, is

$$\kappa_v \sim (3Q_{ext}/4as) \sim 7.1 \times 10^{4}\ cm^{2}g^{-1} \qquad (2)$$

Equations (1) and (2) give $\kappa_v/\ \kappa_{10\ \mu m} \sim 51$. The corresponding ratio inferred from the astronomical data for extinction in the BN star is very similar $(\kappa_v/\ \kappa_{10\ \mu m})_{BN} \sim 50$ (ref. 1). Figure 1 shows that interstellar POM grains could give rise to somewhat weaker, yet probably detectable, features at $\lambda \sim 3\ \mu m$ and $\lambda \sim 16\text{-}23\ \mu m$. The latter feature imparts a further ambiguity to the identification of silicate grains, whilst the former may be confused with the 3.1 μm band of H_2O ice.

Absorbance data for heated POM films[10] may be used to compute an approximate emission spectrum of small POM grains. The absorption efficiency of small particles, irrespective of shape, is proportional to the absorbance γ_{abs} , provided the refractive index n is close to 1 and the absorptive index k remains small throughout the band. Assuming these conditions to be fulfilled the emission spectrum of POM grains may be calculated by

$$F_\lambda = \gamma_{abs}\, B_\lambda(T_g)$$

where $B_\lambda(T_g)$ is the Planck function, T_g is the grain temperature. The emission spectrum of the Trapezium nebula is shown in Fig.2 together with a normalized emission spectrum for POM grains heated to 445K. The agreement is as good as, if not better than, for any silicate model. POM grains are thus able to explain all the available interstellar extinction and emission data.

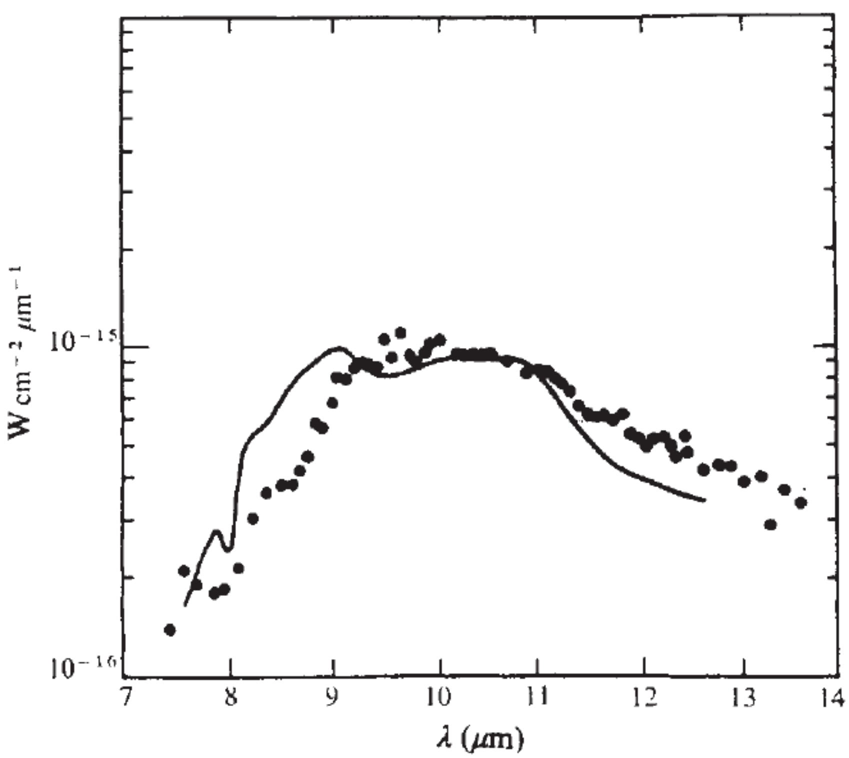

Fig. 2 The infrared emission from the Trapezium nebula compared with the theoretical flux from 445K POM polymer grains (solid curve).

In view of the spectral identifications presented here POM grains must clearly be regarded as a strong candidate for the main component of interstellar dust. Such grains could contribute a significantly higher mass density than silicate grains. More detailed measurements of the complex refractive index of POM (and related polymers) as a function of wavelength and of temperature are required before further comparisons with astronomical data can be made.

Our provisional conclusion is that interstellar grains consist of a mixture of small graphite particles and silicate particles coated with POM-type organic polymeric mantles. The graphite and silicate particles are ejected from cool giant stars; silicate grains have low enough temperatures under interstellar conditions to accrete POM-organic polymer mantles.

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