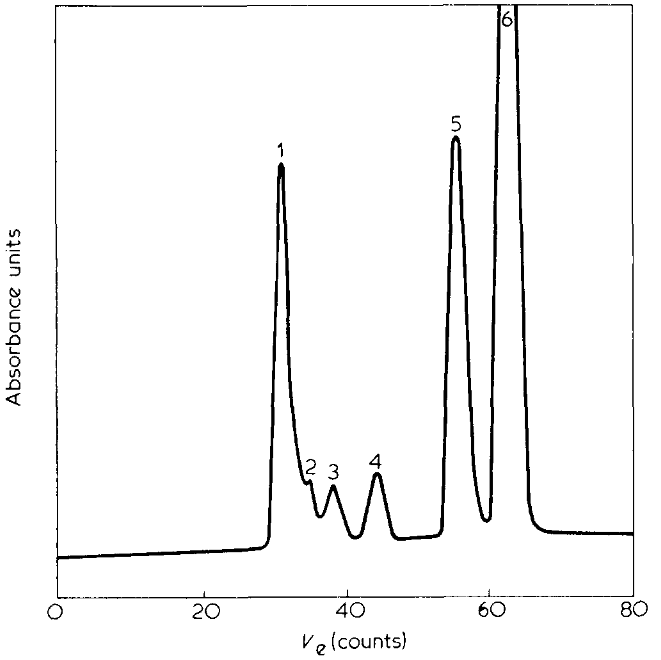
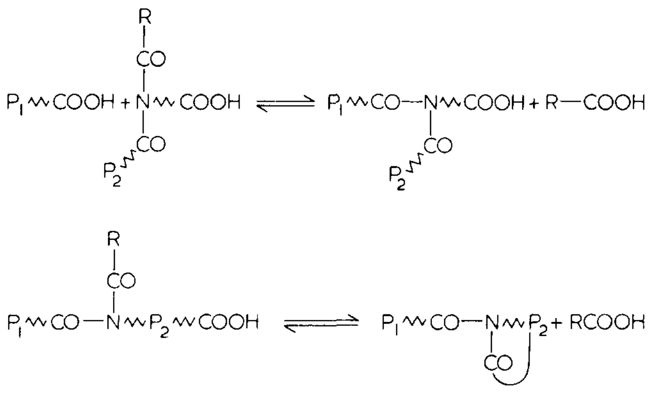


Figure 1 G.p.c. of the reaction product in the solution polymerization of Ib (1.43 mol/kg) initiated with 3 mol% of 4-chlorobenzoic acid in chlorobenzene (2 h/180°C): 1, polymer (M = 2000), 2, 3, 4, oligomers; 5, monomer Ib; 6, chlorobenzene

(chemical shifts 176.183 and 179.63 ppm), while the polymer exhibits only one type of carbonyl (δ = 176.183 ppm).

Aminolysis of 239 mg poly(*N*-benzoyl-8-octane lactam) with 94 mg of benzyl amine in 2.5 ml toluene at 50°C yielded turbidity already within 10 min; within 30 min, a large amount of precipitate was formed indicating deacylation of the polymer accompanied by formation of the unsubstituted polymer of 8-octane lactam. After 17 h of aminolysis/50°C, *N*-benzyl benzamide (m.p. 104°–106°C, ref 8 105°–105.5°C) was isolated from the filtrate.

The polymer of *N*-benzoyl-8-octane lactam (Ia) prepared with 4 mol % initiator possesses a comparatively low intrinsic viscosity (0.106 dl/g, Table 1), which may be due to the formation of branched polymers and macrocycles by inter- and intramolecular acidolysis.



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Infra-red emission studies of thin polymer films

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Polymers can be characterized by infra-red spectroscopy through the variation of their emittance, reflectance or transmittance with frequency. Transmittance is the method most commonly used to identify a material and reflectance is generally used to study the structure of polymers on surfaces[1,2]. Emittance is rarely utilized for the study of polymers because of the experimental difficulties involved[3]. For standard commercial instruments operating at room temperature, the radiation emitted or reflected from the spectrometer and sample holder can be much greater than the emission from a room temperature sample itself especially for thin polymer films.

This communication describes early results using a new method for obtaining emission spectra of thin polymer films with greatly enhanced sensitivity. Competing background radiation and spectral noise are greatly diminished by cooling the spectrometer and sample chamber. An experimental apparatus has been assembled which utilizes this reduced background advantage. It consists of a modified Digilab 296A Michelson interferometer with KBr beam-splitter at 77K, an ZnSe optical collection system also at 77K with the throughput matched to 4 cm^{-1} resolution, and a very sensitive Ge:Cu detector with shortpass cut-off filters operating at 4K. The polymer samples are spun onto freshly deposited metal substrates such as gold or aluminium. The samples are heat sunk to a copper block which is maintained between 80 and 500 ± 1K. Details of the experimental apparatus will be published later.

Typical observed emission spectra are shown in *Figure 1*. The sample was a 4000 ± 500 Å thick film of atactic polystyrene on an aluminium substrate. The film thickness was measured ellipsometrically. A freshly deposited gold sub-

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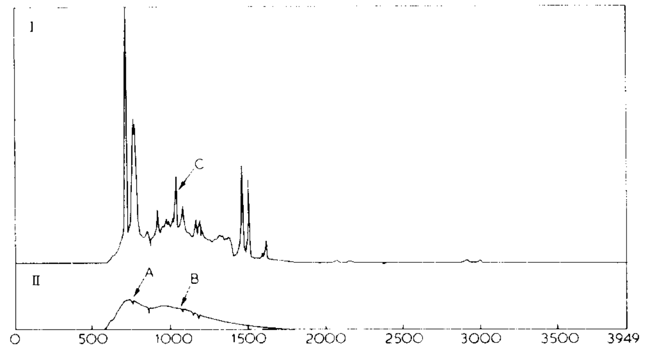

Figure 1 Typical raw emission spectra, 100 scans at 2 cm^{-1} resolution. (I) 4000 Å of polystyrene on aluminium (II) gold reference

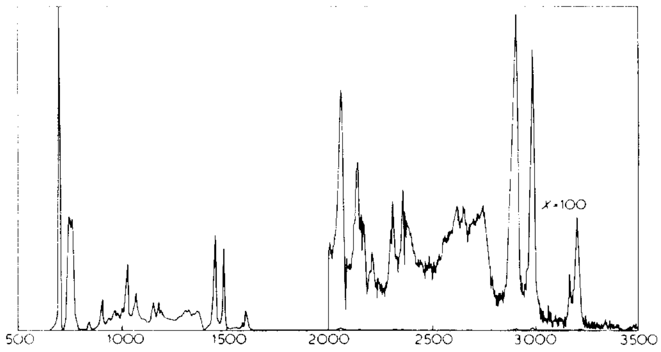

Figure 2 Emission spectrum of 270K polystyrene

strate was used as a reference. Both samples were maintained at the same temperature, 270K. These spectra show three prominent features. There is the 77K background radiation from the spectrometer (A) with a low frequency cut-off determined by optical filters, a broad 270K background from the substrate (B) peaking at about 1000 cm^{-1}, and sharp spectral features (C) due to emission from the polystyrene. Because of the low emissivities of the metal substrates, their background radiation is reduced by approximately a factor of 100. Both sample and reference filled the field of view of the spectrometer and were normal to the optical axis.

The polystyrene spectrum in *Figure 2* was obtained by subtracting the background radiation from the raw spectra and dividing the result by the instrumental response function. The region between 2000–3000 cm^{-1} is expanded 100 times to show the true spectral noise. The observed S/N is approximately 750 for the stronger bands. This spectrum was obtained with 100 scans for each sample or approximately 10 min of collection time. Because of the linear response of this technique it is safe to extrapolate and thus it is possible to measure the infra-red spectrum of a 40 Å polystyrene film with a S/N of 75. Also, since the S/N is proportional to the square root of the number of scans, it can be further improved several fold without taxing the experimenter's patience.

It should be noted that the spectrum qualitatively agrees with the standard polystyrene absorption spectrum but the relative intensities of the peaks differ. The total intensity of radiation emitted by the sample depends upon the probability of spontaneous radiative decay (the Einstein A coefficient) and the number of molecules in an excited state. The observed peaks between 1500 and 3000 cm^{-1} are instrumental artifacts. A fraction of the radiation between wavelengths of 750 and 1500 cm^{-1} is reflected from the detector, passes back through the interferometer and is detected after the second pass.

The relative band intensities in the emission spectrum can be interpreted in terms of the relative absorption coefficients[4]. This has not been done previously because of the inherent difficulties involved. Computer programs are being written to carry out these calculations so that data will be directly comparable with that observed for thicker polymer film in absorption. In addition, spectra have been obtained at various temperatures and angles and will be presented in future papers. Studies are also proceeding with very thin polymer films on reactive metal substrates with the intention of observing interfacial species.

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