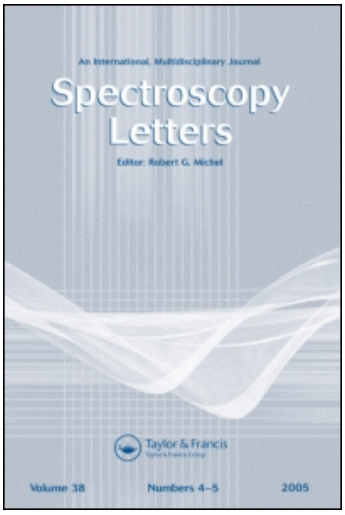

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EFFECTS OF VAPOUR PHASE APPLICATION OF COMPOUNDS TO STRETCHED POLYETHYLENE FILMS

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Abstract: The study shows that aromatic molecules are caught efficiently from vapour phase by stretched polyethylene film and are bonded inside the film showing orientational dichroism. The saturation time is dependent on vapour pressure, degree of vacuum, and temperature. Compared with the usual solution phase method the application of vapour phase offers the following advantages: the film can be more saturated with molecules and micro-samples can be applied with little waste.
The vapour phase application may be a suitable method for studying the bonding mechanism of different molecules with the polymer, e.g. in competition experiments and by concentration effects.
As a special result from this method, it emerges that the strongest transitions of pentacene are all long axis polarized.

This preliminary study tries to make an effect useful, which otherwise is quite a nuisance in the stretched film technique [1] the absorption of aromatic compounds from air into the empty PE-film.
The devices used in our experiments are very simple: the normal holders with empty stretched films, an exsiccator, a vacuum pump, some watch-glasses and a termostatic heater.
One can apply the tiny amount of compound on the watch-glasses and put the holders upon it. Thus a waste of compound is avoided. One can also put the compound directly on the film.

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Then the prepared sample is put into the exsiccator and suitable vacuum, temperature and time are employed - depending on the type of molecule.

In some cases the saturation time can be reduced by putting compound powder directly on the film and adding a few drops of solvent before evacuating the exsiccator.

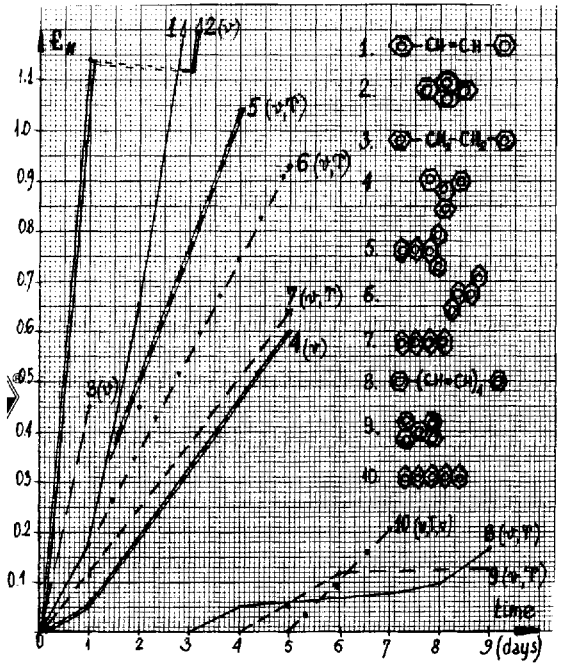

Fig.1 Increasing intensity (E_{II}) of absorption bands during saturation (from vapour phase) on different conditions (v-vacuum - 10mm Hg, T-temperature - 62°C, ▾-drops of chlorophorm on PE-films surface)

Fig. 1 shows E_{II}-values measured for the strongest bands in a series of compounds as function of time of different treatments. One extreme compound is stilbene, shich has a fast increase of E_{II} at room temperature without any vacuum. For pyrene one needs water-pump-vacuum at room temperature in order to obtain E_{II}-values of suitable size in one day. The other extreme is represented by compounds like pentacene, perylene or diphenyl-octatetraene. At room temperature with several days in vacuum no absorption could be observed. But heating the evacuated exsiccator several days to 62°C gave suitable E -values, especially after treating the film surface with solvent.

All other compounds on this diagram are in between these extrema. Thus useful $E_{//}$-values can be obtained for compounds of this sort.

For practical purposes the $E_{//}$-values should also be constant during measurement time. The curves for pyrene, perylene, and diphenyloctatetraene show that the $E_{//}$-values are about constant at least a day, when the films are kept under normal pressure at room temperature.

Thereafter one may as done for pyrene add further compound to the film. One may also "pumpe" the film - that is putting it into an empty evacuated exsiccator - thereby decreasing the $E_{//}$-value. In the case of pyrene "pumping" at room temperature gives this effect, in the cases of perylene and diphenyloctatetraene higher temperatures are needed.

The level of saturation concentration and the time of reaching it are functions of many variables, external ones and molecular properties, which need a more thorough study.

The concentration problem is important with respect to the dichroism observed on samples. In general, we find for each compound the largest dichroism values in the region of about 10^{-4} molarity in our PE-films, giving an indication that this maybe is the concentration of the best orienting sites in this polymer.

In fig. 2 the measurements on diphenylocatetraene and perylene show that increasing the concentration in the same film sample gives a drop of dichroism. The corresponding effect is working in pumping experiments, where decreasing concentration gives increasing dichroism. These results can be explained with the assumption of two different types of bonding sites inside the polymer: one type with stronger bonding and better orientation [2] and another one with weaker bonding and less orientation. Results on films prepared 10 months ago by the solution method are in accordance with the gas phase experiments mentioned above. During this time the films were kept on open air at room temperature. Fig. 3 shows the same tendency for all diphenylpolyenes: decrease of absorption is connected with increase of dichroism.

The differentiation of bonding sites in the polymer according to bonding strength is connected with another question: the relative bonding strength of different molecules. We can report on one preliminary gas-phase competition experiment. Two films containing diphenyloctatetraene and bibenzyl, respectively, were placed at room temperature in an evacuated exsiccator

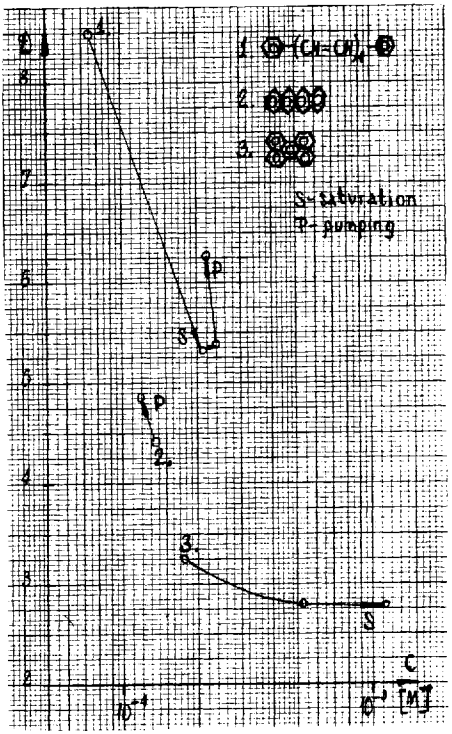

Fig.2 Dichroism v.s. concentration

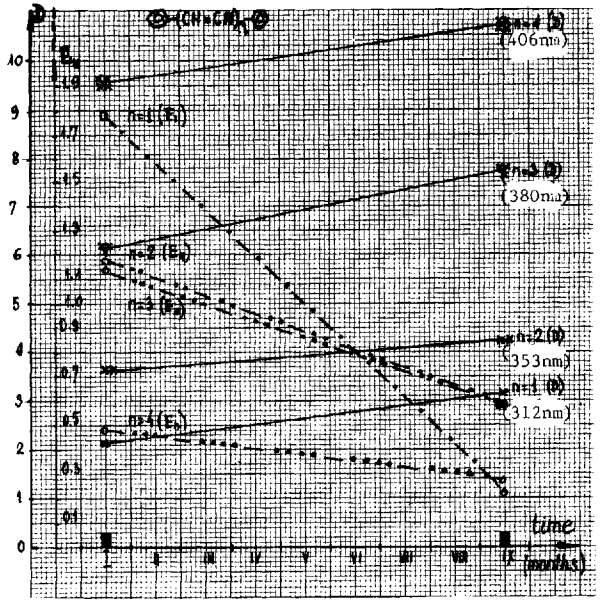

Fig.3 The time dependency of absorption ($E_{\parallel}$) and dichroism (D) for diphenyl-polyenes molecules of type: Ø-$(CH=CH)_n$-Ø in stretched PE-films.(n=1,2,3,4).

together with some stilbene. After three days the first film showed no change in absorption of diphenyloctatetraene and moderate stilbene absorption. The second film showed strong absorption of stilbene and no bibenzyl detectable. Thus stilbene could kick out bibenzyl but not diphenyloctatetraene and the bonding strength sequence is: diphenyloctatetraene, stilbene, bibenzyl.

Finally, we may note that we did not yet check the upper temperature limit of polyethylene in this method. Moreover, other polymers stretchable at higher softening temperatures should be considered. Then one can hope to prepare films with yet larger molecules in measurable concentrations as for example pentacene, where a study of the weaker bands may be possible, after we already with the present technique found the strongest bands all being long axis polarized.

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