

# COMPARISON BETWEEN ENERGY TRANSFER IN LIQUID AND PLASTIC SOLUTIONS

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At the first look a plastic phosphor is not a liquid scintillator, but I want to show that in many fundamental respects it really can be regarded as a scintillating solution.

By their remarkable work Swank and Buck showed that, as in liquid solutions, the energy transfer in plastic phosphors is mainly nonradiative, i.e. not carried out by simple reabsorption of the solvent radiation by the fluorescent solute. Krenz investigated, in particular, solutions of anthracene in polystyrene and showed that the polymerization of styrene is significantly retarded by the presence of anthracene. This led him to the suggestion that the anthracene molecule is somehow attached to the polymer chain. The

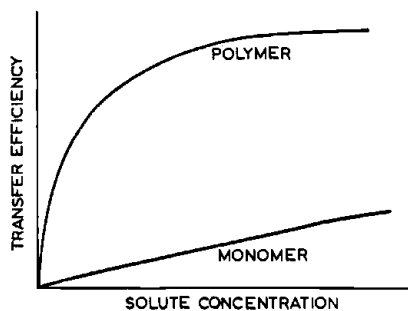


Fig. 1.

possibility thus exists that the energy transfer from the solvent polymer to the solute results from intramolecular processes, i.e. excitation energy being transferred along the polymer chain to the attached fluorescent molecule, rather than from intermolecular processes between solvent and solute molecules distributed at random, similar to those occurring in liquid solutions.

Now, in order to examine this hypothesis, I would say, any hypothesis on energy transfer, we have to use ultraviolet excitation and to determine the transfer efficiency as a function of the parameters involved. The transfer efficiency is defined as the ratio of the number of excited solvent molecules which transfer energy, to the total number of excited solvent molecules.

Now I want to describe briefly the experiments we performed.

First we compared the transfer efficiency of solutions of various concentrations of PPO in *polystyrene* with the transfer efficiency of solutions of the same PPO concentrations in *styrene monomer* (Fig. 1). The differences in transfer efficiency were tremendous.

This striking difference in behavior between monomeric and polymeric solutions would suggest that there is indeed a principal difference between the transfer mechanisms in both systems.

Next we determined the transfer efficiency as a function of time of polymerization, up to 160 hr. The shape of this function is approximately shown in Fig. 2.

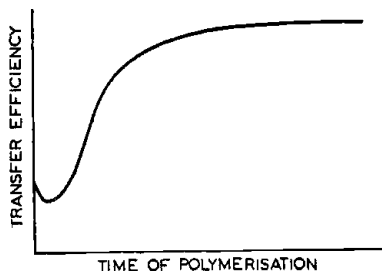


Fig. 2.

At first the efficiency decreases somewhat and then it increases steadily to a fixed value.

Now, in order to examine the *intramolecular* transfer hypothesis directly we prepared two types of solutions. To prepare Type A solution we took a plastic scintillator of anthracene in polystyrene and dissolved it in ethylacetate.

To prepare Type B solution we dissolved pure polystyrene in ethylacetate and added anthracene to the solution.

The relative and absolute concentrations of polystyrene and anthracene for both types of solutions were of course the same.

Now we determined the transfer efficiency for both types of solutions. The results were as follows:

Solid phosphor	Type A solution	Type B solution
78%	19%	35%

It is also interesting to see what happens when the anthracene in the solutions is excited directly by a wavelength not absorbed by polystyrene and not by ethylacetate. In this case the ratio of the intensities of both types is about 30: 26.

If one performs the same experiments with PPO as solute no difference at all exists between Type A and Type B solutions.

## DISCUSSION

The results furnish strong evidence against the assumption that the transfer of energy from polystyrene to the fluorescent molecules (anthracene, PPO) is the result of an intramolecular process. The higher transfer efficiency in Type B solutions with anthracene as solute than in Type A solutions, shows that possible chain attachment is not an essential condition for high transfer efficiency, since in Type B attachment is highly improbable. Moreover, a comparison between the behavior of the plastic phosphor and the Type A solution of the same phosphor yields additional information on the same question. Thus if the energy transfer was essentially due to an intramolecular process taking place along the polymer chain towards the attached fluorescent molecule then only insignificant differences in transfer efficiency should exist between the solid plastic phosphor and the same plastic in solution; since the concentration of such attached plastic phosphor molecules relative to the total number of polymer molecules is not affected by the process of forming solutions of Type A from the plastic phosphor; therefore no change in transfer efficiency between the two systems is to be expected. But if one assumes, on the other hand, a mechanism involving a long range intermolecular transfer process from polystyrene to free solute molecules (or molecules attached to neighboring chains) then obviously the average distances between the donor (polystyrene) and acceptor (PPO, anthracene) is of major importance in determining the transfer efficiency. These distances will be determined, in Type A solutions, by the relative concentration of the plastic phosphor in the solvent. On this hypothesis, therefore, the transfer efficiency in Type A solutions will be less than in the undissolved plastic phosphor, by an amount corresponding to the dilution.

It seems therefore that liquid and plastic solutions are not only phenomenologically similar, but that an intermolecular transfer mechanism, which serves to explain energy transfer phenomena in liquid solutions may well be applicable to plastic systems.

Now, if we accept the conclusion that attachment is not important for high transfer efficiency the question arises why is the transfer efficiency in plastic solutions so very much higher than in the corresponding monomeric solutions. The reason for this may perhaps be found in the structural differences of the monomer and polymer molecules, namely the double bond in the side chain of the styrene molecule, which does not exist in polystyrene.

As can be inferred from the absorption spectrum, each unit of the polymer molecule can be considered as an ethyl benzene molecule. Thus, energy transfer from polystyrene to 2,5-diphenyl-oxazole or anthracene might be considered as similar to the transfer of energy from ethyl benzene to 2,5-diphenyl-oxazole (anthracene etc.). This is essentially the transfer process taking place in the normal liquid scintillating systems, such as, for example,

the transfer of energy from benzene or toluene to *p*-terphenyl, which is well known to be highly efficient.

Although it was shown above that the transfer of energy is not connected with the possible attachment of the solute to the polymer chain, the existence of such an attachment is not, in fact, excluded by the experimental results. As stated before it has been shown by Krenz (and confirmed by the present authors) that the addition of anthracene to the monomer, significantly retards the rate of polymerization. This experimental fact may well support the assumption that anthracene molecules replace free radicals in the polymer chain. If this is true, an explanation that accounts for the differences in energy transfer between Type A and Type B solutions can be suggested: if the transfer efficiency is influenced by the average distances between the excited donor and the acceptor molecules, then it seems reasonable to assume that the diffusion coefficients of either molecule will affect the transfer efficiency. Thus one would expect a decrease in transfer efficiency in Type A in comparison to Type B anthracene solutions, because in the former the mobility of an anthracene molecule is mainly determined by the diffusion coefficient of the huge polymer molecule, to which it is attached, whereas in Type B solutions the anthracene molecules are much more free to move. On the other hand, it was shown that the directly excited fluorescent intensities in Type A solutions are significantly higher than those in Type B solutions. In view of the higher mobility of anthracene in solutions of Type B, this can only be expected, because higher mobility will result in greater selfquenching.

In view of the above considerations, the similarity of behavior of 2,5-diphenyl-oxazole solutions of Type A and Type B is readily understood. Contrary to anthracene, the presence of PPO does not upset the normal polymerization rate of pure polystyrene. It seems therefore that PPO molecules do not tend to attach themselves to the polymer chain, and consequently there should be no reason for difference of behavior between Type A and B.

Finally, the initial drop in pulse height with time during the polymerization process is additional experimental support for an intermolecular transfer mechanism. At first the effect of increasing viscosity of the monomer is predominant. This gives rise to a lower mobility of the solute molecules, which in turn reduces the transfer efficiency. As the polymerization process continues, however, the increasing possibility of energy transfer (because of transformation of the solvent from monomeric to polymeric state) counteracts the effect of high viscosity of the solvent and the transfer efficiency is increased.