STUDIES OF ENERGY TRANSFER AND MOLECULAR MOBILITY IN POLYMER PHOTOCHEMISTRY

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INTRODUCTION

All chemical reactions require rather specific motions of molecules or groups of atoms within molecules in order to take place. One of the attractions of the study of photochemistry is that light-induced reactions usually provide additional information not readily available from thermal reactions about the geometry of the excited states involved in the reaction pathway. If we know the geometry of the most stable or ground state of the molecules involved, we can therefore induce the movements of atoms and electrons which must occur.

The study of the kinetics and mechanisms of gaseous reactions and of small molecules in solution is highly advanced. Very accurate descriptions of the rates of these simple reactions can be described in terms of collision theory and "molecular dynamics". However, a very large number of important chemical reactions occur under conditions where the simple approximations involved in ordinary chemical kinetics are so far away from the real situation as to render their application meaningless. Most biological processes of importance, including photosynthesis, vision and metabolism, occur in systems which involve very large molecules. Here the concept of "billiard ball" collisions between molecules of approximately equivalent size is no longer valid. The random motion of the billiard balls (illustrated in Fig. 1(a)) is replaced by a more coordinated motion when a macromolecule is dissolved or swollen in a solvent (such as water, Fig. 1(b)), and a still further reduction in independent motion occurs when one considers a solid polymer matrix (Fig. 1(c)). Since Nature insists on using macromolecules to carry out processes vital to human survival, the study of these processes is perhaps worthy of some attention. It seems very likely that there may also be special advantages to be gained by using macromolecules in place of their smaller analogues in difficult chemical processes such as in solar energy conversion.
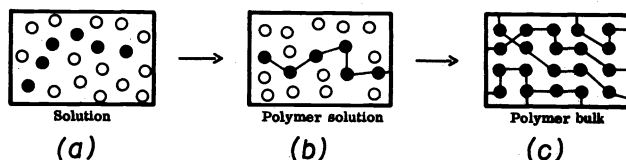

Figure 1

In the present communication I would like to review work carried out in our laboratories at Toronto relating to how the restriction of molecular mobility in polymers (illustrated in Fig. 1) can be expected to affect chemical reactions generally and photochemical reactions specifically, and secondly to illustrate some of the effects which can be expected which are specific to polymer molecules and rarely observed in small molecule analogues.

POLYMER MOBILITY AND CHEMICAL REACTION

Chemists not familiar with macromolecular reactions might assume that the restriction of motion depicted in Fig. 1(c) would be so great that reaction would not occur at all. In fact, this is not the case, and there are now well-authenticated examples of photochemical reactions which are just as efficient in solid polymers as they are in dilute solution of small molecule analogues. On the other hand there are indeed reactions which are completely inhibited in the solid phase. The key to understanding this effect is to know how much movement of atoms is required in order to form the geometry of the excited or transition state and to allow some separation of the products. Reactions differ in their requirements in these respects and if we understand this we are in a position to predict how the reaction will be affected by a polymeric environment. Perhaps the most powerful method of studying such effects involves polymer photochemistry.

Amorphous polymeric matrices indeed provide a very sensitive control of the amount of "free volume" available for a chemical reaction. If we consider a carbon chain polymer, for example, the specific volume curve is given by the solid line in Fig. 2. The dotted line indicates the expansion of the polymer chain with temperature based on bond lengths. The difference in the two curves represents the so-called "free volume" in the matrix.
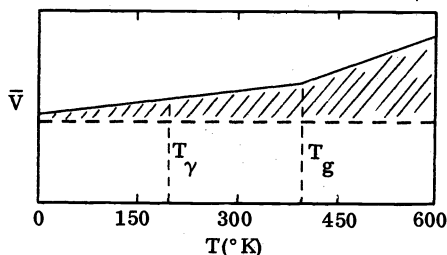

Fig. 2. Specific volume and "free volume" of polymeric material.

At absolute zero there should be, in principle, no free volume, but in fact, because polymer chains can never reach their thermodynamically most favored state (because of viscosity effects) there will be some free volume which can be considered as a contribution from defects in the perfect crystalline lattice. As the temperature then is raised, the amount of free volume increases, and at various positions along the free volume curve, motion of specific groups within the molecule becomes evident. The temperature at which they become visible or observable depends on the frequency of the measurement. The point designated by T_γ in Fig. 2 represents the temperature at which a sufficient free volume is available in polystyrene to observe the movement of phenyl rings at a frequency of about 10 Hz. As the temperature is raised still further, additional free volume becomes available and at the point indicated by T_g a change in the slope of the specific volume curve is observed which is due to the occurrence of motion of very long segments of the polymer chain consisting of units of from 20 to 40 carbon atoms. It can therefore be seen that a polymer matrix provides a relatively continuous increase in the volume available for reactions to take place as the temperature is increased.

Some of the motions which could be important in the occurrence of chemical reactions and physical processes are illustrated in Fig. 3. They include conformational changes of a cyclohexane ring, rotations of a methyl group, rotations of a phenyl group, and diffusion of a small molecule to a large molecule where reaction can take place. The latter, of course, requires the largest amount of free volume to occur.
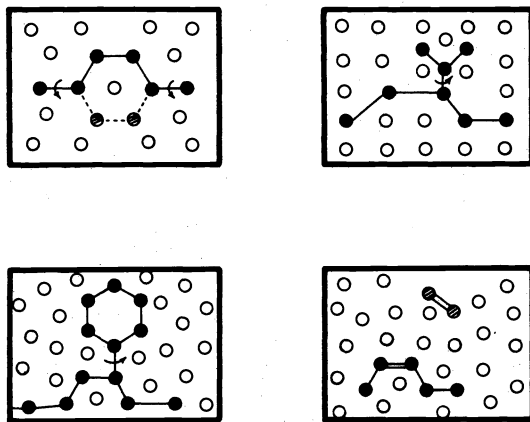

Fig. 3. Some modes of motion required for reaction.

The study of polymeric ketones affords an interesting illustration of the effect of molecular mobility on two types of photochemical reactions, the Norrish type I process which involves a separation of radical pairs, and the Norrish type II which involves an intermolecular hydrogen abstraction by means of a cyclic six-membered intermediate, yielding a biradical which subsequently rearranges to give a ketone and an olefin.(1) In ethylene-carbon monoxide copolymers the formation of the free radical type I products is suppressed because both radicals are polymeric and must escape from the immediate environment.(2) In this case the probability of recombination is quite high and the quantum yield correspondingly low at most temperatures accessible to measurement. On the other hand, ethylene-vinyl ketone polymers, the photolysis of which yields one polymeric and one small acetyl radical, gives a very high efficiency of type I product because the same amount of free volume will permit substantial diffusion of the small acetyl radical away from its larger polymeric counterpart.(3) In polyethylene at room temperature the quantum yields for this process can be as high as 0.5.

Both the lifetime of the triplet excited state and the quantum yield of the Norrish type II process in polyethylene at room temperature are comparable to those in hydrocarbon solution under the same conditions. This somewhat surprising result is due to the fact that at this temperature polyethylene is well above its glass transition and hence very large movements of segments of the chain are possible although there is no net motion of the center of mass of the polymer. These motions permit the formation of all the necessary conformations for reaction within the lifetime of the excited state. If, however, the polymer is cooled down, the frequency with which the excited state can be reached is reduced and the quantum yield begins to drop off below -40° C and reaches 0 at -120° C, the glass transition of polyethylene.(1) At this temperature no further molecular motion is possible within the lifetime of the excited state and the reaction is completely eliminated.

A similar effect is observed in the photolysis and radiolysis of 7-tridecanone which is a crystalline solid melting at 33°C. Irradiation of the crystals at 10°C shows no observable type I or type II products. On the other hand, if the crystals are melted, the quantum yields are comparable to those of the ketone in solution at the same temperature.(4) Obviously in the crystalline lattice, there is not sufficient mobility either for the escape of radical pairs formed by the type I process nor the formation of the cyclic intermediate required for the type II.

The photolytic behavior of vinyl ketone copolymers can be measured very precisely because, as illustrated in the scheme below, the Norrish type II process results in the scission of the backbone of the polymer chain.
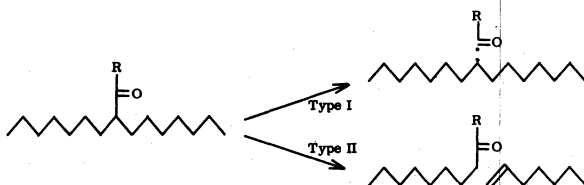
The quantum yield for this process is given very simply by the expression:

$$\phi_{cs} = \frac{1}{I_A}\left[\frac{1}{(\overline{M}_n)_t} - \frac{1}{(\overline{M}_n)_0}\right] \tag{1}$$

where $M_n(0)$ is the initial number average molecular weight of the polymer and $M_n(t)$ is the number average molecular weight after absorption of I_A quanta of light. The use of automatic viscometry permits a very precise measurement of the quantum yield.(5) Typical data on a methyl methacrylate–methyl vinyl ketone copolymer at various temperatures in toluene solution are seen in Fig. 4.(6) The temperature dependence observed in this case represents a contribution to the total activation energy due to the energy barriers of rotation of the carbonyl group about the center of the polymer chain. Normal Arrhenius plots are observed in this case with activation energies corresponding to a value of about 4 kcal/mole.

If, however, the photochemical reaction is carried out in the solid phase, as shown in Fig. 5, there is a relatively small increase in the quantum yield at low temperatures, but a drastic increase in the region of the glass transition temperature.(7) Above the glass transition temperature, the quantum yield for the type II process is identical to what it was in solution at the same temperature, again illustrating the increase in mobility occurring at this transition.
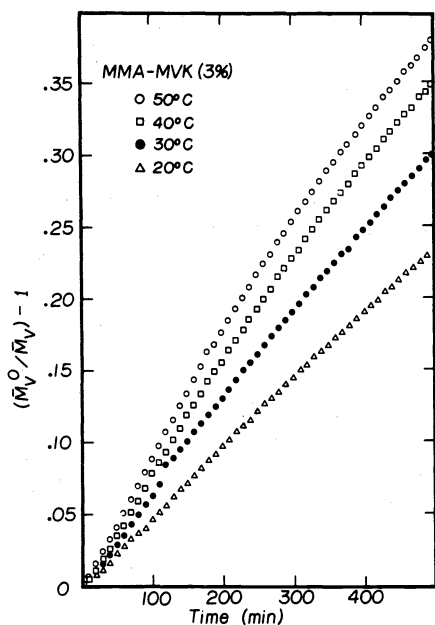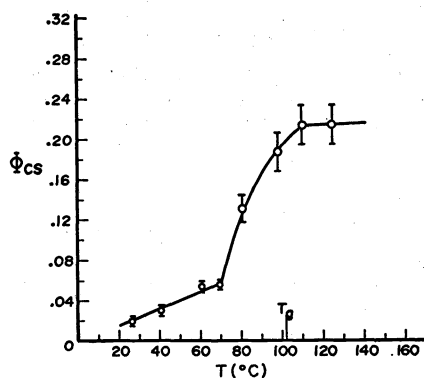
Fig. 4. Solution photolysis of
MMA-MVK copolymer.

Fig. 5. Quantum yields in
solid MMA-MVK.

It would be tempting to predict that all photochemical reactions might show this drastic increase at
the glass transition temperature, but this is not the case. The reason for the large temperature coef-
ficient in the latter case is due to the fact that rather large changes in the conformation of the poly-
mer molecule are required in order to form the cyclic six-membered intermediate for the type II
process. On the other hand, studies of the photoFries reaction in solid polymer matrices indicate
that in this case there is very little effect due to the glass transition temperature.[8] The photoFries
reaction, shown schematically below, apparently proceeds by means of a "caged radical" mechanism:
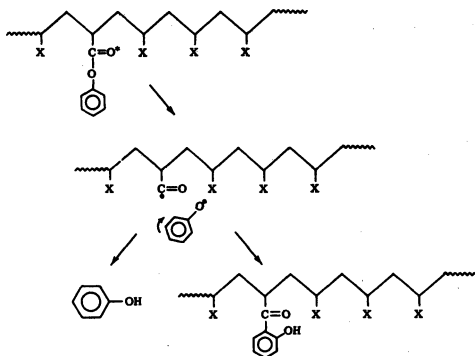
In this case only a small rotation of the phenoxy radical intermediate is necessary to provide for the
rearranged product yielding an acetophenone from the original phenyl ester. The quantum yields for
this process in poly(phenyl acrylate) are comparable to those of phenyl acetate, both in solution and
in solid phase at a temperature well below the glass transition of the polymer. This is illustrated in
Table 1. There appears to be no wavelength dependence of the quantum yield for this reaction, sug-
gesting that it proceeds from the same, presumably singlet, excited state. However, the activation
energy for the formation of the para product (1.8 kcal mole^{-1}) is slightly larger than that for the
ortho Fries product (1.2 kcal mole^{-1}) which suggests that slightly larger spatial requirements are
necessary in the latter case. An Arrhenius curve for the ortho product is shown in Fig. 6. Another
interesting reaction which occurs with considerable efficiency in the solid phase is the Paterno-
Büchi reaction between excited benzophenone and polyisoprene. Irradiation of a film of polyisoprene
containing benzophenone results in the formation of hindered diphenyl oxetane rings attached to the

TABLE 1. Quantum yields for photoFries products

	Solvent	ϕ_o	ϕ_p
Phenyl acetate	Cyclohexane*	0.18	0.20
Phenyl acetate	Cyclohexane*	0.17	0.15
Phenyl acetate	1,2-Dichloroethane	0.18	0.22
Poly(phenyl acrylate)	1,2-Dichloroethane	0.12	0.23
Poly(phenyl acrylate)	Solid film (air)	0.10	0.13
Poly(phenyl acrylate)	Solid film (N_2)	0.10	0.14

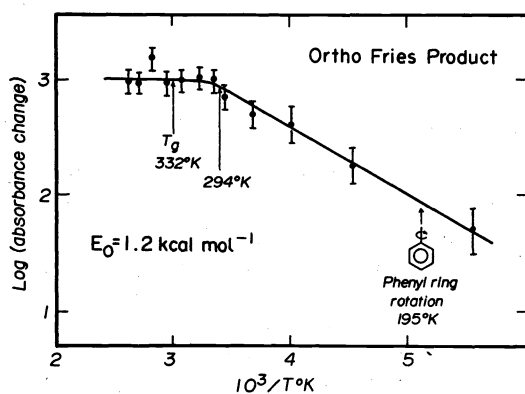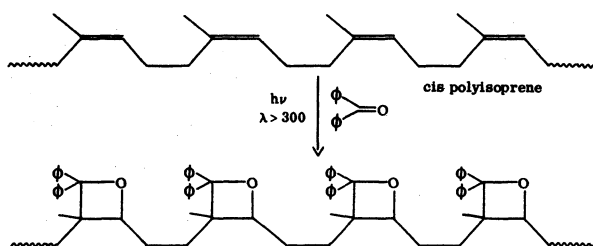Note: $\lambda_{ex} = 250$ nm; T = 23° C; $T_g = 59$° C
*Shizuka et al.

Fig. 6. Arrhenius plot for photoFries reaction in poly(phenyl acrylate).

double bonds in place of the double bonds of the polymer.(9) Although in principle it would seem possible to synthesize a structure similar to that given below,

there is a physical limitation due to the fact that the introduction of hindered rings increases the glass transition of the polymer up to a point where the benzophenone is no longer soluble in the polymeric matrix. The increase in glass transition is quite remarkable and is shown in Fig. 7. The reaction appears to take place with equal facility up to this point in either solution or the solid phase.
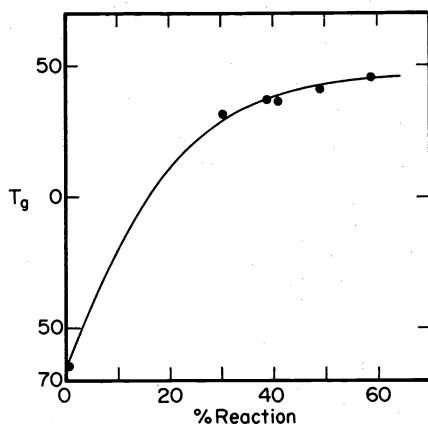
Fig. 7. Glass transitions for polyisoprene-benzophenone photo adducts.

ENERGY TRANSFER IN POLYMERS

The problem of energy transfer in polymeric materials is of particular interest because a variety of energy transfer processes are possible. Intermolecular energy exchange can take place by transfer of energy from small molecule chromophores to those on a polymer chain, as illustrated below or,
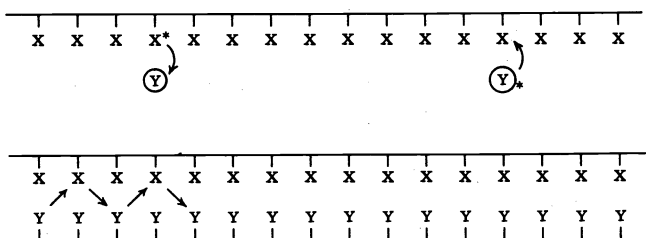
alternatively, the excitation energy from a chromophore on a polymer can be transferred to a small molecule. One can also envisage exchange between two polymer molecules. An even more interesting type of energy transfer involves energy exchange along polymer chains by the process shown at the right. These include energy hopping from group to group along a polymer chain, exciton band migration along the backbone of polymer chains, and energy migration along a chain and hopping across loops in the polymer chain in solution. Examples of all these types of energy exchange are now well documented in polymer systems.
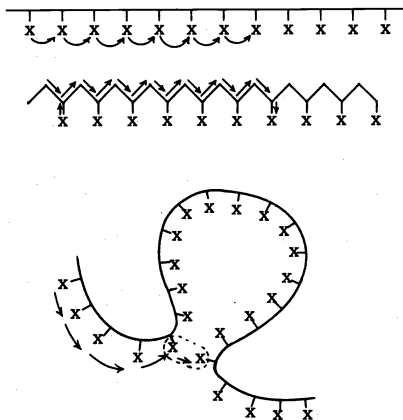
In early studies we showed by measurements of the type II process in polyethylene-carbon monoxide that the triplet reactions could be quenched by cyclooctadiene at approximately collisional rates in dilute solution, and also in the solid phase.(10,11) In this case the limiting rate is the diffusion of the cyclooctadiene through the amorphous polyethylene matrix. Studies of the quenching of type II photolysis of poly(phenyl vinyl ketone) showed that substantially all the reaction arose from the excited triplet state and that the quantum yields and lifetimes were dependent upon sequence distribution in phenyl vinyl ketone-styrene copolymers.(12) That is to say that the photochemistry of the vinyl ketone group depended on whether or not it was isolated or in a long sequence of similar units. Energy exchange along the polymer chain was invoked to explain these results. Studies of the γ-radiolysis of ethylene-carbon monoxide copolymers also gave strong evidence for energy migration along the C—C backbone by an exciton band mechanism.(13)

When ketone or naphthalene groups are included in polymeric chains by copolymerization, very interesting effects are observed when the phosphorescence of solid films is studied at low temperatures. (14) Arrhenius plots for the phosphorescence of polystyrene copolymers are shown in Fig. 8.
The sharp change in slope of the Arrhenius plots occurs at the γ-transition of the polystyrene, which indicates the very strong role which the mobility of the phenyl ring plays in the quenching of phosphorescence of groups in the immediate vicinity. This appears to be due to a combination of the effects of oxygen diffusion and the conformational mobility of the polymer chain. The phenomena shown in Fig. 8 are quite general and may be used to identify the temperatures at which particular forms of molecular motion begin in solid polymer films. Figure 9, for example, shows typical data for rotation of the phenyl ester in films of poly(phenyl acrylate). It is also worth pointing out that poly(methyl methacrylate) is not a rigid glass below its glass transition temperature. Substantial motions of the ester, ester methyl, and α-methyl groups occur at temperatures as low as $-200°\,C$.
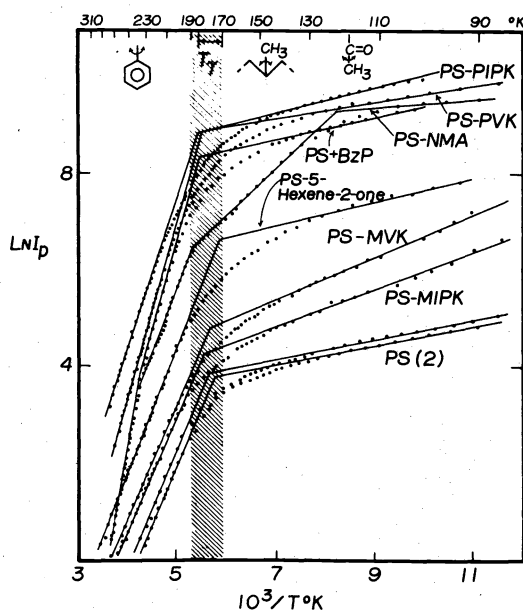

Fig. 8. Phosphorescence of
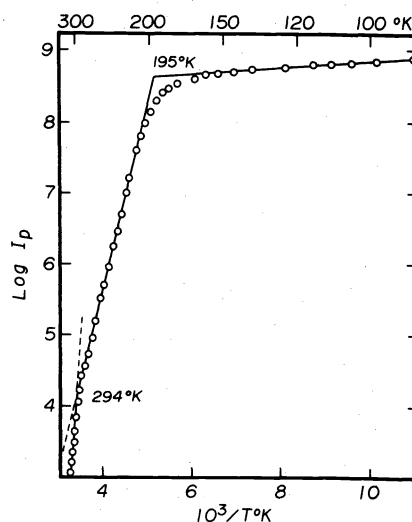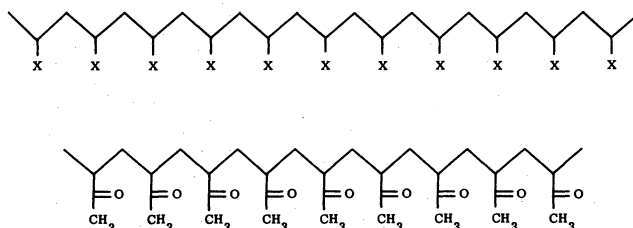styrene copolymers.

Fig. 9. Phosphorescence of
poly(phenyl acrylate).

A problem which has interested us for some time is the mechanism by which energy can exchange along a polymer chain by a collisional mechanism. (15, 16) This is illustrated in the scheme below for poly(methyl vinyl ketone).

Although energy exchange between the excited triplet of a ketone and another ketone group is not energetically favorable, it does occur in a certain proportion of all collisions. The problem in a molecule of this kind is defining exactly what a collision is. Can one think of a lining up of the molecules so that the carbonyl groups are essentially in collision at all times, or is it necessary for chain rotations to allow collisions between either adjacent or next nearest neighbors during the normal random motion of a polymer in solution?   As an approach to the solution to this problem, we have collaborated with Professor Turro's group at Columbia University in measuring the rate of energy exchange between excited triplet acetone and carbonyl groups on a methyl vinyl ketone-styrene copolymer using the automatic viscometer referred to previously. (17) The precision of the automatic viscometer apparatus permits the measurement of extremely small changes in molecular weight and therefore of reactions which have relatively low probability. In this case the excited triplet energy of the acetone when transferred to the ketone carbonyl induces the type II photolysis of the polymer

chain, resulting in a chain scission. The data shown in Fig. 10 show the results of a kinetic treat-
ment which relates the number of scissions in the polymer chains to the first order rate of decompo-
sition of dioxetane. The total change in the flow times measured in the viscometer for this experi-
ment was only of the order of 300 msec, but the precision is such that an excellent first order decay
curve is obtained. The kinetic treatment of these data, along with quenching experiments using cyclo-
octadiene allow the calculation of the rate constant for transfer from triplet acetone to vinyl ketone
groups on the polystyrene chain to be $0.5 \times 10^6 \, \ell \, mol^{-1} \, sec^{-1}$, which is of the same order as that ex-
pected for the transfer to acetone itself. The problem of determining how rapidly the exchange occurs
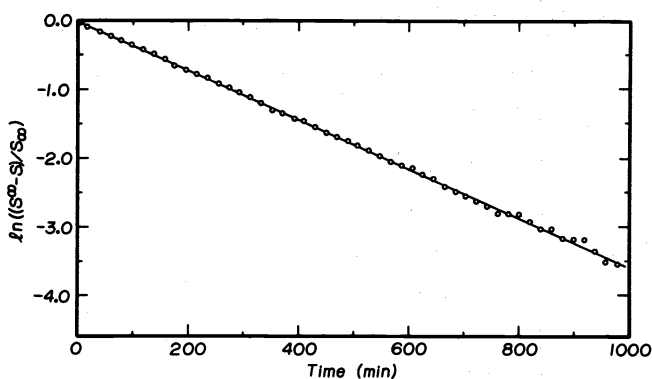along a polymer chain in this instance still remains to be solved.

Fig. 10 First order rate curve for sensitized
photoscission of MVK-styrene copolymer.

Energy exchange by hopping or exciton mechanisms along polymer chains is much easier to observe
experimentally when the chromophores have longer lifetimes than ketone triplets or singlets. This
has prompted a number of studies involving polymers containing naphthalene or other polynuclear
aromatic chromophores. Poly(naphthyl methacrylate), for example, shows rather efficient migration
of both singlet and triplet energy along the naphthalene groups in the same chain. Triplet energy
transfer is illustrated by the occurrence of delayed fluorescence from triplet-triplet annihilation in
dilute glasses at liquid nitrogen temperatures. (18) However, singlet migration can be shown very
clearly via fluorescence studies in highly dilute solution. Poly(naphthyl methacrylate) shows excimer
emission at high dilution in organic solvents and the ratio of monomer to excimer fluorescence is
independent of concentration over a very wide range of concentrations. However, the ratio does de-
pend upon whether or not the solvent expands the chain. In a good solvent, such as chloroform, the
chain is highly expanded and the amount of excimer fluorescence is reduced. A poor solvent, such
as ethyl acetate, shown in Fig. 11, on the other hand causes a compact chain which shows enhanced
excimer fluorescence. This suggests that an appreciable portion of the excimers are formed, not
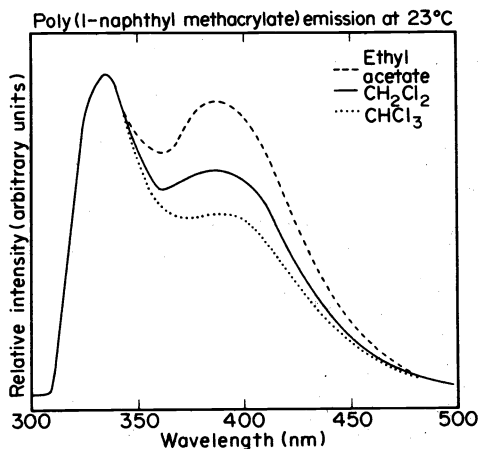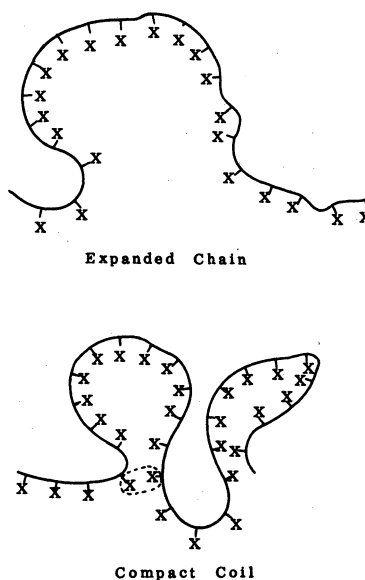

Figure 11

from adjacent naphthalene groups, but by crossing
over of groups at a loop in the random coil, as
shown at the right. Excimers are, of course, not
generally observed in small molecules at these
very low concentrations.

A polymer chain containing repeating chromophores
can be considered in some respects as being anal-
ogous to a one-dimensional crystal. Depending on
the chain's stiffness and dimensions, these groups
can be maintained within rather similar and con-
trolled distances from each other. Energy ex-
change along such chains can be, in some cases,
quite efficient. This results in the occurrence of
a phenomenon which Professor George Porter has
described as the "antenna effect". It is well known,
for example, that traces of anthracene in a crystal
of naphthalene will fluoresce with considerable ef-
ficiency whenever the naphthalene is irradiated.
We have recently prepared copolymers of naphthyl
methacrylate with vinyl anthracene in which the
latter group represents only 0.05 mol-% of the total
polymer. The molecular weights are such that
there is on the average only about one anthracene
group per polymer chain. When such a polymer is dissolved in a suitable solvent and the naphthalene
groups are irradiated, extensive energy migration occurs between the naphthalene groups followed by
transfer to the anthracene and emission of anthracene fluorescence.(19) The relative intensities of
naphthalene and anthracene fluorescence are independent of concentration over a very wide range of
dilution (Fig. 12) and it seems clear that the energy transfer observed is intra- rather than inter-
molecular. This effect could conceivably be used to collect light energy from extended regions of
solution at high dilutions and transfer it to a chemical group capable of inducing a chemical reaction
rather than emission. Such a process might have considerable relevance to problems relating to
solar energy conversion.

Expanded Chain

Compact Coil

Emission from poly(l-naphthyl methacrylate co 9-vinyl anthracene)
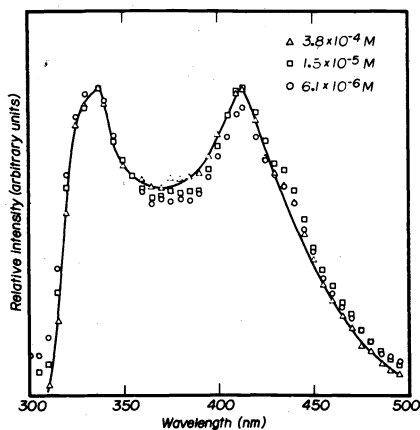(CH$_2$Cl$_2$ at 23°C)

Figure 12

In conclusion it has been demonstrated that polymer photochemistry provides useful insights into the free volume required for the occurrence of both thermal and photochemical reactions. It seems possible that additional understanding in this field may well lead to selective control of reactions by the use of polymeric matrices. The problems of energy migration and exchange in polymeric molecules are both interesting and challenging and lead to phenomena which may well be unique to polymeric systems.

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