PHOTOTRANSFORMATION OF POLYMERS

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ABSTRACT

This survey deals with the photochemical reactions of macromolecules and is given mainly from the point of view of organic polymer chemistry. Photocrosslinking is of great practical importance and even though there are a great number of patents and publications in this field only the most important principles are briefly discussed. Another topic is photoaddition with polymers and photoisomerizations. Our own experiments dealt with the addition of fluorene or ring ethers to unsaturated polyesters, the addition of maleic anhydride or maleimides to polystyrene, the isomerizations of polyesters and polyamides with azobenzene groups in the backbone, and finally with rearrangements of chlorinated polyhexamethylenadipamide (nylon 66). In addition the photoinitiated polymerization of di-ynes and tri-ynes and the photocondensation of bisazides are discussed.

INTRODUCTION

There are many different approaches to apply the basic principles of photochemistry to polymer science. If we consider only the molecular weight of the starting materials and of the end products in a photochemical process (irrespective of kinetics, mechanism, quantum yield or possible intermediates) the following four reaction types can be distinguished.

$$a + b \xrightarrow{h\nu} c \qquad (1)$$

$$m \xrightarrow{h\nu} P \qquad (2)$$

$$P \xrightarrow{h\nu} n + m \qquad (3)$$

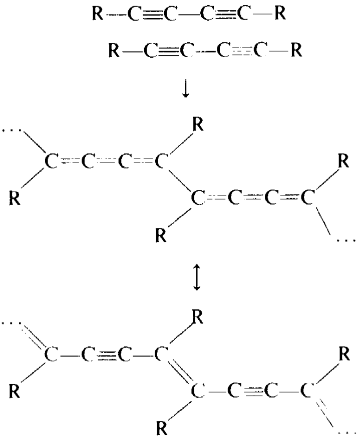
$$P \xrightarrow{h\nu} P' \qquad (4)$$

In these schematic equations small letters represent the low-molecular compounds, P and P′ are polymers.

In reaction type 1 the starting materials (a and/or b) as well as the end product c are low-molecular compounds; this schematic equation describes the wide field of preparative organic photochemistry. This is not the subject of the following review, but it should be mentioned that polymers can act as sensitizers in these reactions[1], a fact which may be of great importance in biological photoreactions.

In reaction type 2 the starting materials are low-molecular compounds, and the formation of polymer P proceeds by a photoreaction. The so-called 'photoinitiated polymerizations' which have been thoroughly examined, belong to this general type. They have been described in many reviews[2, 3]. Usually m is a vinyl compound or an acrylic acid derivative. In the photoreaction an active species is formed, i.e. a radical or a radical ion, and this initiates the propagation of the monomer m by a chain mechanism. The growing chain propagates by a dark reaction.

A completely different case of photopolymerization, which also belongs to the reaction type 2 but differs substantially from the examples mentioned above, is the topochemical photopolymerization of derivatives of 2,4-hexadiyne-1,6-diol, examined by Wegner[4]. The reaction can be described by the equation (5) and consists of a 1,4-addition of the conjugated triple bonds.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During this reaction a polymer is formed with three cumulated double bonds per base unit or the mesomeric en-yne structure. It must be emphasized that this polyreaction can only proceed in the crystal state. As the packing of the molecules in the crystal lattice is very important for the topochemical reaction, the ability to polymerize depends primarily on the type and size of the substituents. The phenylurethanes and tosylates of the diyne-diol are easy to polymerize, while the benzoates do not polymerize at all.

The resulting polymers are completely crystalline. Due to the conjugated double bonds the crystals of the polymers are deeply blue-violet, red or purple in contrast to the complete lack of colour of the monomer crystals. Therefore photopolymerization can be observed in changes of the absorption spectra. Quite recently Kiji[5] was able to synthesize the homologous tri-yne-diol (I).

$$\mathrm{ROCH_2{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OR} \qquad \text{(I)}$$

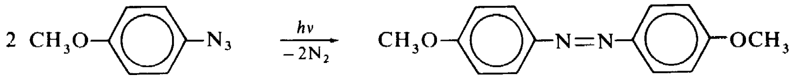
$\mathrm{R{:}H;\ CO{-}NH{-}C_6H_5;\ CO{-}NH{-}C_4H_9}$

$\mathrm{OC{-}C_6H_5;\ SO_2{-}C_6H_4{-}CH_3}$

The diol and some of its derivatives can also be polymerized by means of light in the crystal state. The photosensitivity is even larger. The polymers are also deeply coloured. Their chemical and crystal structure are under investigation, but we can conclude from preliminary results that the polyreaction proceeds via a 1,4-addition.

The photoaddition reactions systematically studied by De Schryver[6] and Hasegawa[7] are basically different from these photoinitiated polymerizations. Here the polymer is not formed by a chain mechanism but by a step mechanism, i.e. each step of addition requires a new photoprocess. The same is true for polymer formation by means of photoreductive coupling of bis-benzal imines[8] or diketones[9].

Bössler[10] tried to produce polymers by repeating a kind of photocondensation. The basis of this reaction is the formation of azo compounds during the photolysis of special aromatic azides [equation (6)].



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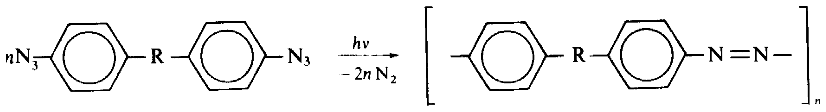
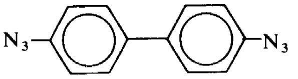


(7)

Experiments by Horner *et al.*[11] showed that the yield of pure azo compounds depends on the solvent and the substituents of the azide. Starting from suitable bis-azides one should obtain polymeric azo compounds [equation (7)]. The following bisazides (II) and (III) have been prepared[10].



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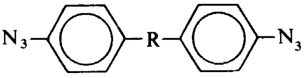


(III)

$R = O\text{—}(CH_2)_2\text{—}O$

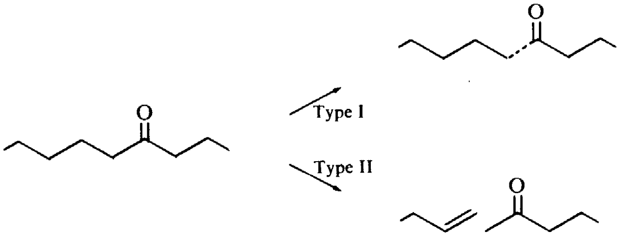
$O\text{—}(CH_2)_{10}\text{—}O$

When these colourless substances were irradiated in an organic solution or in water suspension nearly the theoretical amount of nitrogen was formed and intensively coloured products were obtained. Unfortunately most of them were so insoluble that the determination of molecular weight was impossible. Although one knows that polyazo compounds prepared in a different way[12] are also insoluble, it is thought that in this case the side products formed during the photolysis of the azides caused an additional crosslinking.

Nevertheless it was possible to extract soluble fractions from some polymers with dichloroacetic acid. Because of halochromism these solutions are deep red or deep blue. The absorption spectra have sharp maxima at 518 mμ and the model compound azoanisole shows the same spectra in dichloroacetic acid. Therefore it can be concluded from this that during photolytic condensation, polyazo compounds were actually formed, but nothing is known about the side reactions that lead to the crosslinking or interruption of the condensation.

PHOTODEGRADATION

Reaction type 3 is the inverse of reaction type 2 and describes the photochemical degradation of polymers producing a mixture of oligomers, the monomer or other low-molecular products. These reactions are not only interesting from the theoretical point of view, but are also of great practical importance. Recent results of photodegradation have been described by Grassie[13]. A lot of research is devoted to the problem of the inhibition of photodegradation and the development of photostabilizers for plastics, lacquers, rubbers and fibres. Frequently the degradation reactions are very complex processes, because they are accompanied by autoxidation, crosslinking, rearrangement etc.[14]. Pure photolytic degradation based on reactions of Norrish Types I and II have been examined by Guillet *et al.*[15] with keto-group-containing polymers [equations (8) and (9)].



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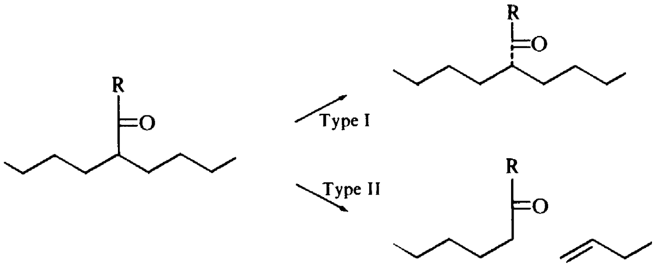

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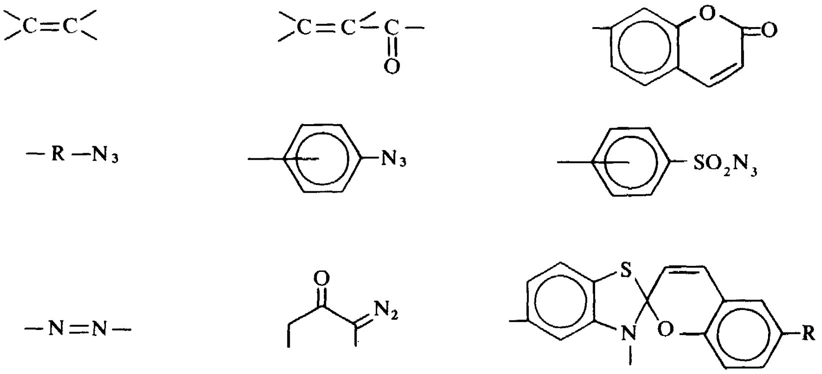
MACROMOLECULAR PHOTOCHEMISTRY

In equation (4) at least one component of the starting materials as well as the reaction product are macromolecular substances and the reaction consists of a photochemical transformation of the polymer. This field can be called 'macromolecular photochemistry'.

The pre-requisite of such reactions is that the polymer P shall contain photosensitive groups in the main chain or in sidechains. These groups can occur in every repeat unit of the polymer (when the highest possible concentration is present) or in smaller amounts, statistically distributed along the polymer chain. Some examples of photosensitive groups, which have already been inserted into polymer chains, are shown in *Scheme 1*.

Scheme 1. Photosensitive groups in polymers.



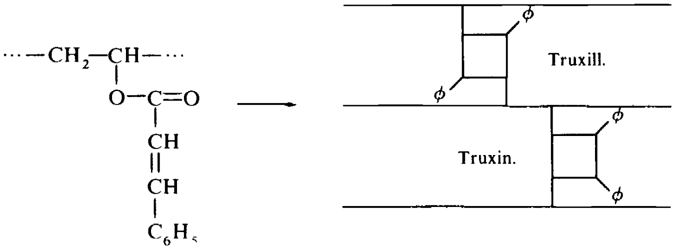
The macromolecular backbone can be produced by conventional methods such as polymerization, copolymerization, polycondensation or polyaddition. The photosensitive groups can either be included in the monomeric starting compounds or inserted into a given polymer.

It has been shown that in some cases there is no difference in the photoreaction if the sensitive group is bound to a macromolecular frame or to a small molecule, which means that the polymer photoreaction and the model reaction proceed in the same manner. Nevertheless there are many examples for specific polymer effects, e.g. rate, quantum yield, reaction mechanism, byproducts etc. are not identical with the analogous reaction in small molecules. It can be of great importance if the photoreaction of the polymer takes place either in solution, in the solid state, above or below the glass-transition temperature, in the crystal state or in an ordered matrix. Reactions of type 4 are usually accompanied by large changes of physical properties of the polymers, for instance light absorption, solubility, viscosity etc.

(a) Photocrosslinking

Often the soluble polymer P changes during irradiation into a crosslinked and insoluble polymer P′. We call this kind of reaction ‘photocrosslinking’. These reactions have been examined in detail, because they are of great economic interest for image forming, production of printing plates, relief images, printed and integrated circuits (especially in microelectronics). There are many reviews of the theoretical basis and practical application of phocrosslinking polymers[16]. Therefore only a few examples will be mentioned.

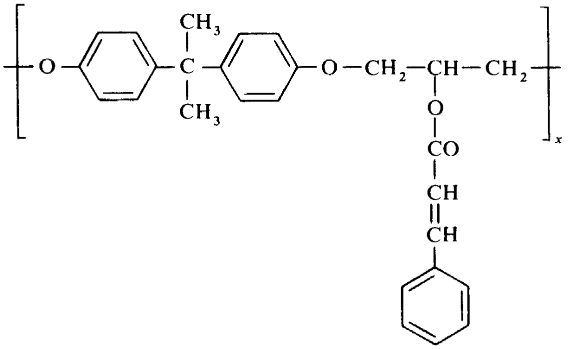
Many crosslinking reactions are based on the well-known photocyclodimerization of cinnamic acid or its esters, forming substituted cyclobutane derivatives ('truxillic' or 'truxinic acids'). Many ways of preparing polymers with pendant cinnamic acid groups have been described, for instance by esterification of hydroxyl polymers (polyvinylalcohol, cellulose, epoxide resins) with cinnamic acid. The basic reaction of crosslinking is schematically shown in equation (10).



(10)

The formation of α-truxillic groups has been proved experimentally[17]; however, it has to be assumed that other types of crosslinking occur with the highly reactive radical intermediates. IV to VI are other photocrosslinkable polymers with pendant cinnamic acid groups, chalcone groups or cumarin groups, respectively. Different polymers with stilbazole groups have also been prepared.

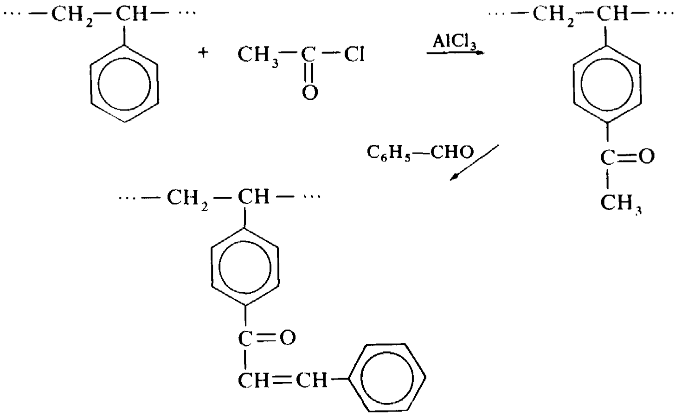
The most important problem is to get a sufficiently high photosensitivity; therefore in general specific sensitizers must be added.



(IV)

Another way of achieving photocrosslinking is based on the photolysis of azides. In this reaction nitrenes of great reactivity are formed which react by insertion, addition or substitution. From the large number of azide group containing polymers only a few example will be mentioned [equations (11), (12); polymers VII to X]

The azidoisocyanates XI to XIV described by Holtschmidt and Oertel[18] make new photosensitive polymers available.



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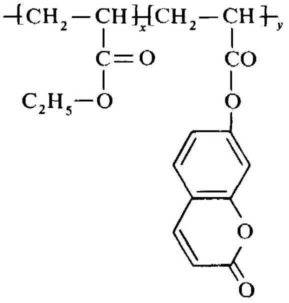

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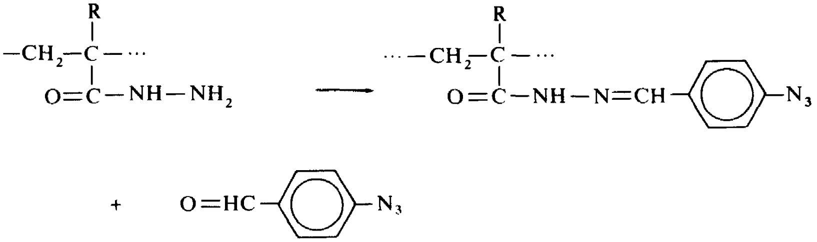

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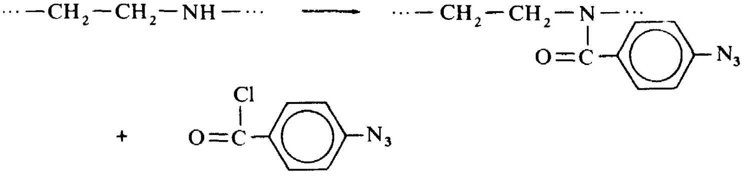

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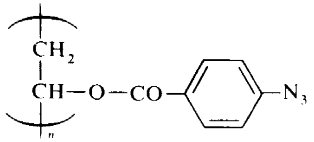
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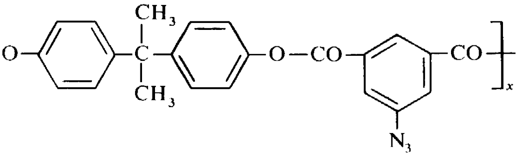
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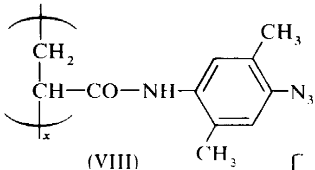
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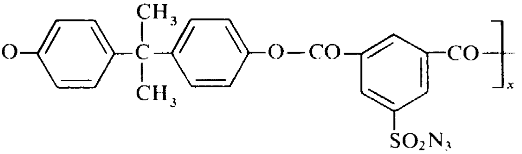
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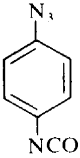
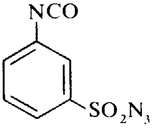
(XI)
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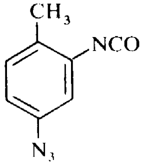
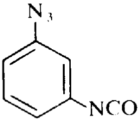
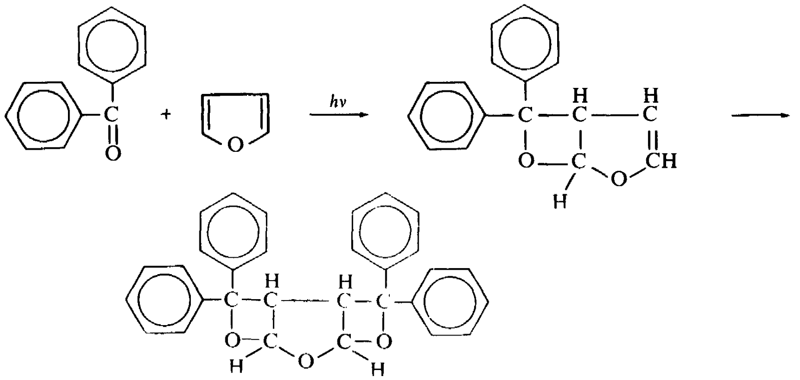



(XIV)

(b) Photoaddition to polymers

During the photoreactions described above only insoluble polymers were produced. However, there are some known phototransformations in which no crosslinking takes place, and the starting polymers P and the end products P′ are soluble.

Although many photoadditions with low-molecular compounds have been described, only a few have so far been used to produce macromolecules. In an earlier paper[19] we described a Paterno–Büchi reaction between polyvinylbenzophenone and furan or benzofuran [equation (14)] which according to experiments by G. O. Schenk *et al.*[20] should lead to the formation of oxetane groups [equation (13)]. The assumed structure was proved spectroscopically. The conversion was approximately 80 per cent. In this case the photosensitive group was part of the macromolecule and a low-molecular compound contained the activated double bond.



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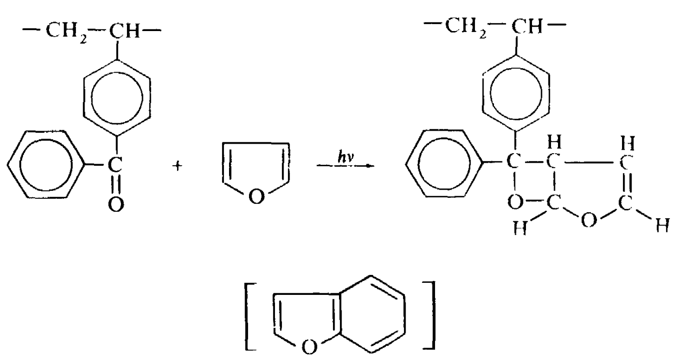
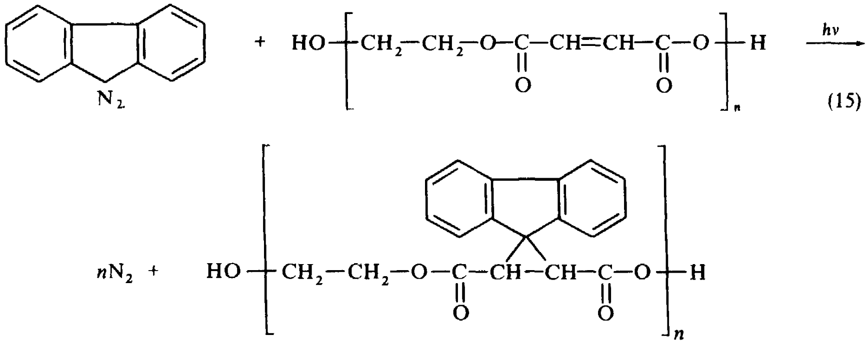


(14)

The next example [equation (15)] shows the opposite case where the activated double bond is part of an unsaturated polyester. It was prepared in the usual way by melt-polycondensation from maleic anhydride and ethylene glycol, and was a viscous resin with about 93 per cent of the theoretical number of double bonds, 71 per cent of which existed in the *trans* configuration.

When diazofluorene is photolysed a carbene is formed. When this reaction is carried out in the presence of an unsaturated polyester the carbene adds to the double bond forming a spirocyclopropane group[21].



(15)

To a dilute solution of the unsaturated polyester in benzene slightly more than the equivalent amount of diazofluorene was added. Upon irradiation with a mercury vapour lamp at a temperature of 4° to 6° C nitrogen was formed and the deep red colour of the reaction mixture gradually disappeared. The polyester used was a viscous, tacky material whereas the product of the photoaddition was a solid, powdery substance with a softening range between 145° and 180° C. In the i.r. spectrum both aromatic bands and bands typical of cyclopropane rings appeared at 11.6 and 9.6 μ. The n.m.r. spectra corresponded to those of model compounds and confirmed the assumed structure.

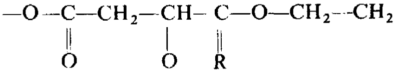
The degree of conversion resulted from determining the number of remaining double bonds. We found that about 90 per cent of the double bonds had been consumed. It should be mentioned that because of the spiro-structure the plane of the fluorene group is perpendicular to the main chain. One can demonstrate with space-filling models that the flexibility is therefore considerably reduced.

The fluorene group in these polymers is a strong π-donor and together with an acceptor such as tetracyanoethylene (TCNE) or tetracyanoquinodimethane (TCNQ) polymeric charge transfer complexes are formed. Because a photoisomerization of the double bonds takes place during the photoaddition, the polymeric photoadducts contain *cis*- and *trans*-cyclopropane units. In order to examine the polymeric CT-complexes, we prepared the same polyester starting from the pure monomer, *cis*- or *trans*-spirofluorene cyclopropanedicarboxylic acid[22]. The spectral properties of these polymers and their ability to form charge transfer complexes were identical to those of the photosynthesized polymers. These results indicated that the two polymers had the same chemical structure.

Some years ago Rosenthal and Elad[23] described the benzophenone-sensitized photoaddition of ring ethers and cycloacetals to the double bonds of ethyl maleate and ethyl fumarate. After thorough investigations the authors proposed a radical mechanism which, however, will not be discussed here. It has not been ascertained whether a charge transfer complex, like the one between THF and maleic anhydride, is involved here. The photoaddition is probably accompanied by a *trans–cis* photoisomerization. Earlier work by Hammond *et al.*[24] showed that with acetophenone as sensitizer at 28.5°C a photostationary state exists with 80.3 per cent of the ethyl maleate.

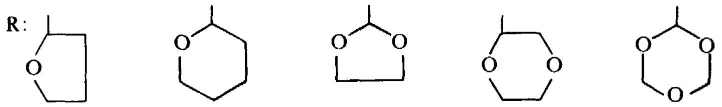
We have applied this photoaddition to the unsaturated polyesters[21] mentioned above. The other reactants were: tetrahydrofuran, tetrahydropyran, 1,3-dioxolane, 1,4-dioxane or trioxane. These compounds actually served as both reactants and solvents; they were therefore used in large excess (40 to 60 mol ring–ether per mol C═C). After addition of 1 to 10 mol acetophenone per mol repeating unit of the polyester, the clear solutions were irradiated at 50°C with a mercury vapour lamp. The experiments with trioxane were carried out at 70°C, in order to get a homogeneous melt. After about 20 to 25 hours by precipitation with ether 50 to 75 per cent of the polymer was recovered. The i.r. and n.m.r. spectra of the polymeric photoadducts corresponded with those of the model compounds and we concluded that a polyester of the structure XV was formed.

The total conversion was determined by the addition of *n*-dodecylmercaptan to the remaining double bonds and it was found that 90 to 95 per cent of the double bonds had been consumed. During the photoaddition of tetrahydropyran a crosslinking took place and part of the polymer became insoluble. The other photoadducts were readily soluble. In contrast to the starting products they are solids and their softening range—depending on the adduct —was between 110° and 145° C. The viscosity numbers were also considerably higher than those of the starting product. However, the spectra also showed a small content of phenyl groups; acetophenone is probably incorporated by a side reaction.

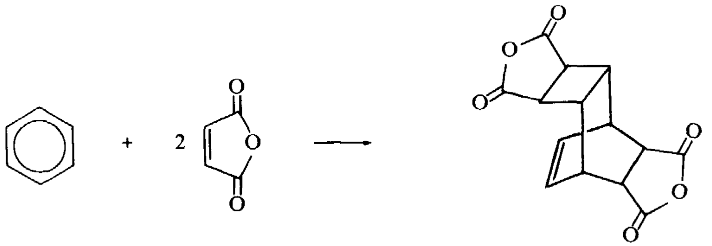


$$-O-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{|}}{CH}-\underset{\underset{R}{\|}}{C}-O-CH_2-CH_2$$

(XV)



The next example concerns a photoaddition to aromatic double bonds. Some years ago Bryce-Smith *et al.*[25] described the photoreaction between benzene and maleic anhydride. If one irradiates maleic anhydride in a benzene solution in the presence of benzophenone or acetophenone, a compound with the structure (XVI) precipitates as a white solid.



(XVI)

It was shown that the reaction proceeds by the excitation of a charge-transfer complex. Apart from this the steric conditions were also very important for adduct formation. If one wants to extend the reaction to a polymer, the question of a suitable solvent arises. No photoadditions with polystyrene have been observed in cyclohexane. Chloroform or carbon tetrachloride are suitable, but after long irradiation a crosslinking of the polystyrene took place. The best results were obtained with a large excess of acetophenone (the sensitizer), as solvent. After an irradiation time of 5 to 72 hours the polymer was precipitated and purified by several reprecipitations. The softening point of the polymer was about 175° C and was about 50C° higher than that of polystyrene. The viscometric molecular weight diminished only slightly from 300000 to about 240000. In the i.r. spectrum new characteristic bands appeared at 1870 and 1790 cm^{-1} (*Figure 1*) which are also present in the photoadduct of benzene and maleic anhydride. It can therefore be assumed that the irradiated polystyrene does indeed contain base units of structure XVII.

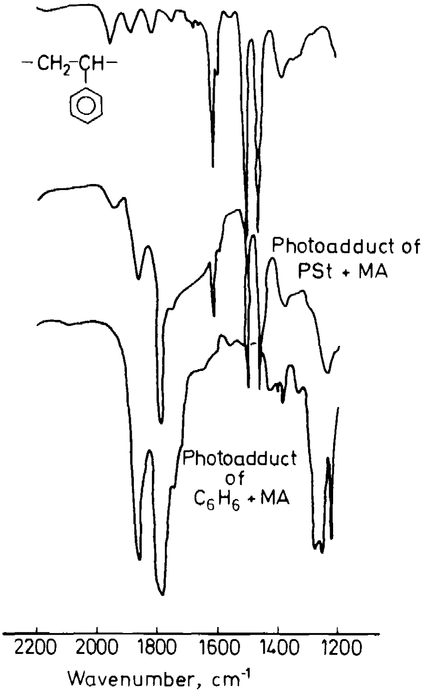
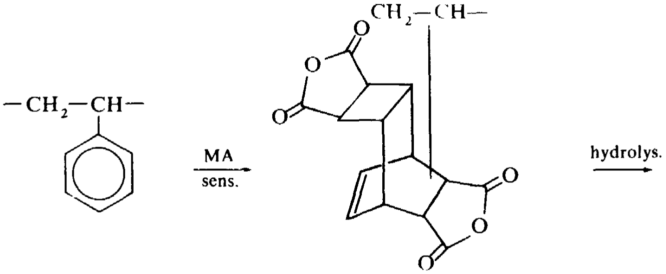


Figure 1. The i.r. spectra of polystyrene (above), photoadduct of polystyrene and maleic anhydride (middle), and photoadduct of benzene and maleic anhydride (below).



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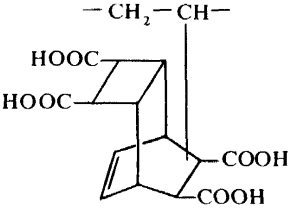


(XVIII)

It is not known which C atom of the ring system is attached to the polymer backbone, but it is likely to be one of the vinylidene group. In order to determine the amount of base units XVII, the polymer was treated with an alcoholic potassium hydroxide solution and the carboxyl groups XVIII formed during the saponification were titrated. On the basis of the assumed structure, a content of 21.5 weight per cent of these groups was calculated. From the oxygen analysis of the anhydride (XVII) and of the free acid (XVIII) form, contents of 20 and 22 wt % respectively of the above-mentioned groups were found. Because of the high molecular weight of the substituents this corresponds to a conversion of only 8 mol %. The reason for the low conversion is definitely steric hindrance, which is even larger in the polymer than in the comparable models of toluene, ethylbenzene and cumene. Here also lower yields than with unsubstituted benzene were found.

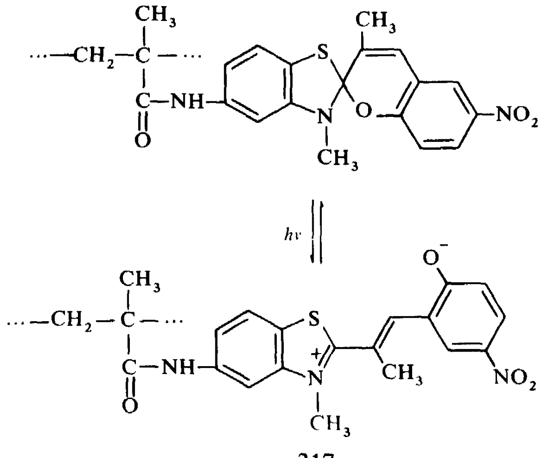
Since maleimide[25] also adds photochemically to benzene, we have extended this reaction to polystyrene. Under similar conditions polymers were formed, the i.r. spectra of which indicated that in fact a photoaddition took place. After an irradiation of 12 hours there was a reaction of only 4 mol % (calculated from the nitrogen content). In addition there was much insoluble polymer.

The experiments described show that photoadditions of polymers with aromatics are possible in principle, but both limitations in solubility, and steric effects, hinder the reaction.

(c) Photoisomerizations in polymers

Another group of interesting photoreactions are isomerizations caused by light. They can consist of a *cis–trans* isomerization, a rearrangement, a shift of bonds or a migration of substituents.

In low-molecular compounds such photoisomerizations have been known for a long time and have been thoroughly examined. During the last few years corresponding reactions with polymers have also been described. Of particular interest are isomerizations accompanied by a clear change of colour and therefore called 'photochromism'. Smets *et al.*[26] have produced a number of polymers which have spiropyran groups as photochromic groups (for instance, on the basis of substituted methacrylamide, XIX).

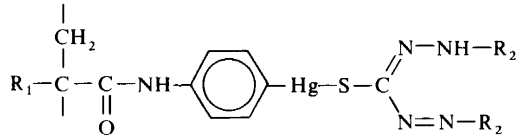


(XIX)

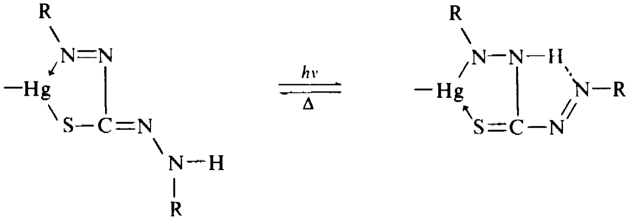
Apart from this, various polycondensates were prepared in which the photochromic groups are in the main chain. Another polymer was prepared with pendant photochromic groups on a polytyrosine backbone.

Under irradiation, these polymers become coloured because a coplanar system of double bonds results from the opening of the spiran ring. In the dark the colour fades again. The authors were able to show that the rate of the dark reaction depends mainly on whether the polymer was in solution or in the solid state (film).

Kamogawa[27] also investigated the synthesis and properties of photochromic polymers. This work deals with the photoisomerizations of mercury thiocarbazonate groups (XX).



(XX)



Under irradiation the complex rearranges and the original maximum at 488 mμ decreases in intensity and is replaced by a new peak at 580 mμ. In the dark the stable form reappears. The isomerization proceeds in a dioxane solution and also in cast films. However, the half-life time both for the photoreaction and the dark reaction are considerably longer in the film than in solution.

Another group of photoisomerizations are the *trans–cis* rearrangements of polymers with C=C double bonds. For example, Voigt[28] examined the isomerization caused by u.v. light on unsaturated polyesters containing different amounts of fumaric acid or maleic acid units. The polymers were irradiated as films of about 0.1 mm thickness at 30° C, in the presence of air. The irradiated polymers were hydrolysed and the amount of maleic acid or fumaric acid was determined polarographically. It was shown that the photostationary equilibrium is mainly on the side of the maleic acid.

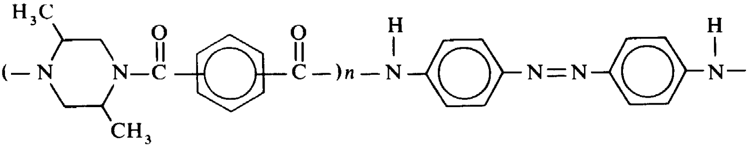
Other investigations have been carried out on the photoinduced *cis–trans* isomerization of 1,4-polybutadiene and 1,4-polyisoprene. The change of the microstructure was shown in the n.m.r. and i.r. spectra. Golub *et al.*[29] found that photocyclization occurs as a side reaction during the irradiation, with the consequent formation of cyclopropyl groups.

It is known that aromatic azo compounds can also be converted from the stable *trans*-conformation into the *cis*-conformation by irradiation. This reaction has also been extended to many polymers. The azo groups can be located either in the main chain or in the pendant groups of the polymers. Lovrien[30], for example, irradiated the aqueous solution of a copolymer of methacrylic acid and *N*-(2,2′-dimethoxyazobenzene)-acrylamide. During this reaction the viscosity of the solution changed markedly. This photoviscosity effect is explained by the change of the form of the macromolecules which was caused by the *trans–cis* isomerization of the azo groups.

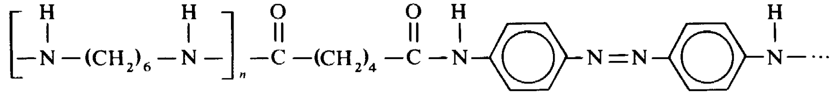
Kamogawa *et al.*[31] prepared numerous polymers with pendant azobenzene groups (for example substituted polyacrylamidomethylaminoazobenzene). During the irradiation the *trans*-form partly rearranges into the *cis*-form. The extent of rearrangement can be calculated from the change of the absorption spectrum. In the dark the *trans*-form is reformed. Here again one observed that the thermal reverse reaction proceeds much more slowly in the film than in a benzene solution.

Another example has been described by Goodman *et al.*[32] who incorporated a small amount of azo groups into optically active polypeptides and studied the changes of the Cotton effect under irradiation.

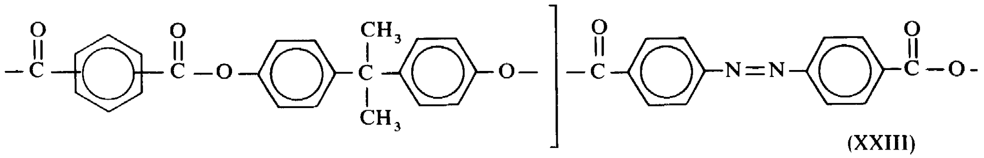
In a recent paper, Morawetz and Paik[33] described polymers with azoaromatic groups either in sidechains or in the main chain. The former are copolymers of methacrylic ester or styrene with *p*-*N*-(methacrylyl)-aminoazobenzene. The latter are copolyamides (XXI, XXII) or copolyesters based on bisphenol A (XXIII). The content of azo groups was very low, somewhere between 0.6 and 1.4 mol %.



(XXI)



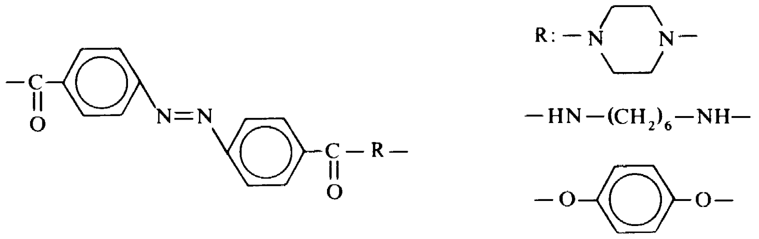
(XXII)



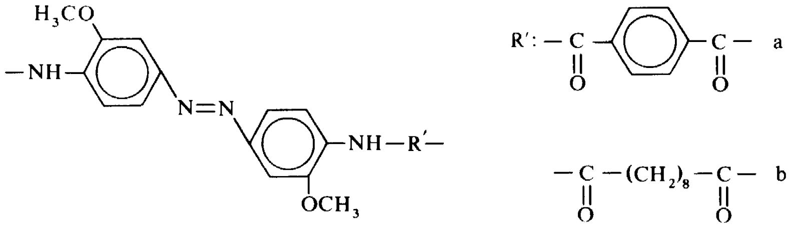
(XXIII)

The photochemical *trans–cis* and the thermal *cis–trans* rearrangements were studied both in solution and in bulk. It was shown that the rate of isomerization and the photostationary states depend primarily on the reaction conditions—whether it takes place in solution or in the solid state, or above or below the glass transition temperature.

In our own experiments we wanted to test if (a) in the *cis–trans* isomerization in polymers there is a cooperative effect and (b) if during the isomerization the form of the macromolecules changes to such a degree that an obvious change of the physical properties results from it (e.g. solubility, viscosity, elasticity, T_g etc.). For this purpose we needed polymers with the largest possible number of azo groups in the main chain. As mentioned above, pure azobenzene polymers are insoluble. B. Löhr[34] therefore prepared polyamides and polyesters starting from azobenzene dicarboxylic acid and diamino azobenzene by interfacial polycondensation. Unfortunately here, too, most of the polymers were so difficult to dissolve that they could not be used for the experiments we were planning. Only the polymers XXIV and XXV were soluble in hexafluoroisopropanol or *m*-cresol. Furthermore the corresponding low-molecular model compounds were prepared in order to compare the spectra and the kinetics of the isomerization. The absorption of the *trans*-azo bond is sensitive to both substituents and solvents and is located between 320 and 400 mμ. If the solutions of the polymer or the model compound are irradiated by monochromatic light (366 mμ) the intensity of the *trans* band greatly decreases (see *Figure 2*).



(XXIV)



(XXV)

The irradiations were stopped when the *trans* content had decreased to about 50 per cent. Then the dark reaction, leading again to the all-*trans* form, was followed at different temperatures. The isomerization proceeded exactly according to first order kinetics. Some examples are shown in *Figure 3*.

The rate constant, of course, also depends on the substituents and the solvents. However, if we compare the polycondensates with the analogous model compounds under identical conditions we cannot find significant differences in the rate constants and activation energies. Some data are listed in *Table 1*. From these results it follows that each azo group isomerizes independently and obviously there is no cooperative effect. Probably the distance between the azo groups in the chain is so great that no interaction takes place.

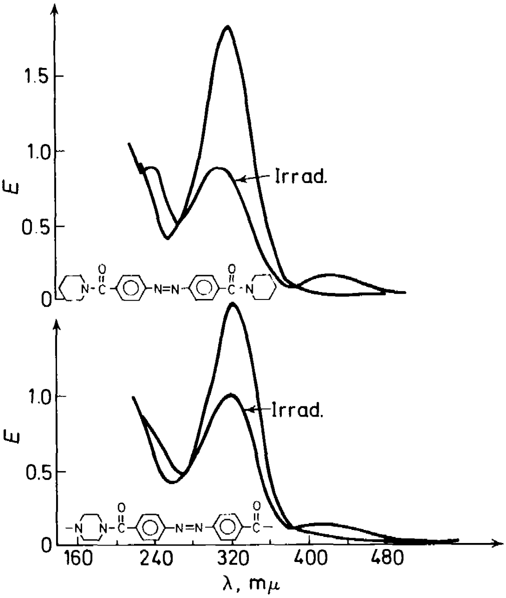


Figure 2. Absorption spectra of model compound and polymer XXIVa before and after irradiation. Solvent: hexafluoroisopropanol.

We could not find out if other physical properties besides the absorption were changed by irradiation because we could not produce any films from these polycondensates. Since the flexible segment between the azobenzene groups is too long, we can conclude that the isomerization cannot contribute much to the shape of the macromolecules.

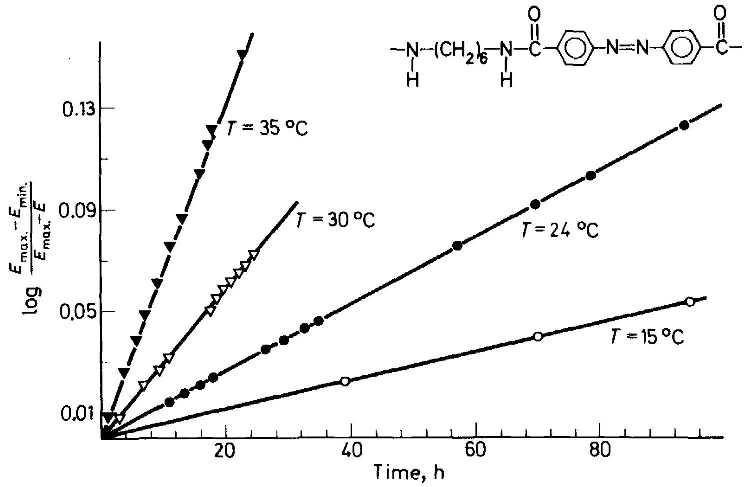
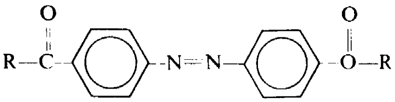
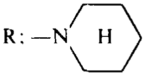
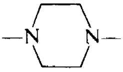
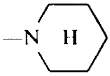
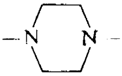
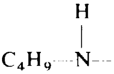
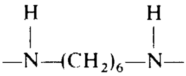
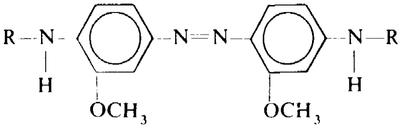
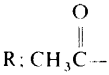
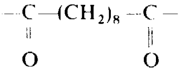
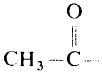
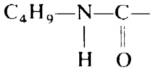
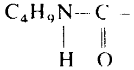


Figure 3. First order plot of the thermal *cis–trans* isomerization of polymer XXIVb at different temperatures. Solvent: hexafluoroisopropanol.

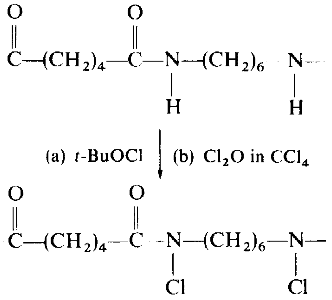
Table 1. Rate constants of *cis*–*trans* isomerization of some polymeric azocompounds and models

	solvent	λ_{max} (nm)	$k \times 10^7$ (sec^{-1})	t (°C)
	Hexa-fluoro-isopro-panol	318	2.76 9.3 21.4 40.5	15 24 30 35
	Hexa-fluoro-isopro-panol	318	2.4 7.2 17.3 45.4	15 24 30 35
	*m*-Cresol	329	187	22
	*m*-Cresol	329	192	22
 $C_4H_9-N(H)-$	Hexa-fluoro-isopro-panol	318	3.7 9.1 19.3 45.4	15 24 30 35
 $-N(H)-(CH_2)_6-N(H)-$	Hexa-fluoro-isopro-panol	318	3.6 8.3 18.2 41.5	15 24 30 35
				
 R: $CH_3C(=O)-$	*m*-Cresol	386	17960	24
 $-C(=O)-(CH_2)_8-C(=O)-$	*m*-Cresol	395	9900	22
 $CH_3-C(=O)-$	Dioxane	385	380	22
 $C_4H_9-N(H)-C(=O)-$	*m*-Cresol	403	17400	22
 $C_4H_9N(H)-C(=O)-$	Dioxane	402	2080	22

(d) Photorearrangements in polymers

Here some preliminary results of Schuttenberg[42], Turner[41] and Müller, concerning photorearrangement of *N*-chloro-polyamides, will be discussed.

The well-known low-molecular *N*-halamides such as *N*-bromosuccinimide are very reactive compounds. In connection with our extensive experiments on polymers with functional groups[35], we attempted to produce polymers with *N*-halamide groups. Indeed we succeeded in replacing the H-atom on nitrogen with a Cl-atom in numerous polyamides[36]. Conversions for this reaction were normally between 30 and 95 per cent of theoretical conversion. The following details, however, are limited to nylon 66. Suitable chlorinating agents are for example tert. butylhypochlorite (dissolved in tetrachloroethane), chlorine monoxide, or aqueous solutions of hypochlorous acid [equation (17)]. The conversion can be determined by the amount of chlorine contained in the polymers. The structure of *N*-chloro nylon (XXVI) is confirmed by the i.r. and n.m.r. spectra. Since there are no NH groups, no H-bonds can be formed. Therefore *N*-chloro polyamides have low softening points and are soluble in many organic solvents, for instance, *N*-chloro nylon is soluble in chloroform or benzene. Like the corresponding low-molecular *N*-halamides it is an oxidizing agent[37]. By the oxidation of potassium iodide to iodine we can quantitatively determine the content of *N*-chloro amide groups in the polymer. Organic compounds, such as sec. alcohols, hydroquinone, leucodyes, mercaptans, thioethers etc, can be oxidized under very mild conditions and the reaction can be carried out either in organic solvents or in a heterogeneous system. *N*-chloro-nylon is therefore appropriate for use as a polymeric reagent[38]. In this manner it can be applied as a reactive support in columns. Because during the oxidation reactions the amide group is reformed, those reactions which start in solution result in the formation of insoluble polyamide.



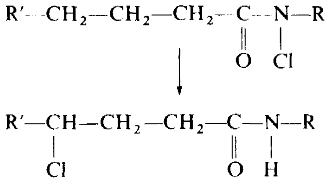
$$\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-(CH_2)_6-\underset{\underset{\displaystyle H}{|}}{N}-$$

$$\text{(a) } t\text{-BuOCl}\ \Big\downarrow\ \text{(b) } Cl_2O \text{ in } CCl_4 \qquad (17)$$

$$\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Cl}{|}}{N}-(CH_2)_6-\underset{\underset{\displaystyle Cl}{|}}{N}- \qquad \text{(XXVI)}$$

In the course of these experiments we observed that *N*-chloro nylon rearranges at higher temperatures or by irradiation. It is known that under irradiation in the presence of strong acids, *N*-chloramines are converted into 4-halo-alkylamines, which are changed into other final products (for example, by spontaneous cyclization into pyrrolidines), according to the different experimental conditions. This reaction is called the Hofmann-Löffler reaction and there are many preparatively interesting applications[39]. A radical chain mechanism is assumed but photophysical or photochemical details are not known yet.

A rather similar rearrangement also takes place during the irradiation of *N*-halamides[40] [equation (18)]. In the case of the *N*-chlorocarboxyamides the 4-chloramides formed are very stable and can be obtained in good yields. These conversions are carried out in organic solvents mostly at room temperature. According to the conditions a more or less large amount of the unsubstituted amide is also formed. Although this reaction is of synthetic interest and many examples have been described, the photochemical aspects have yet to be studied systematically. In spite of this we have tried to extend this reaction to the *N*-chloro nylon described above.



$$\mathrm{R'{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{\textstyle O}{\|}}{C}{-}\underset{\underset{\textstyle Cl}{|}}{N}{-}R} \;\longrightarrow\; \mathrm{R'{-}\underset{\underset{\textstyle Cl}{|}}{C}H{-}CH_2{-}CH_2{-}\underset{\underset{\textstyle O}{\|}}{C}{-}\underset{\underset{\textstyle H}{|}}{N}{-}R} \qquad (18)$$

R′:alkyl; R:t-C_4H_9

N-chloro nylon was dissolved in hexafluoroisopropanol (concentration six per cent) and the solutions were irradiated in Pyrex ampoules in a high vacuum with the unfiltered light of a medium pressure mercury vapour lamp. The decrease of the *N*-chloro-amide groups was followed by iodometric titration. Under these conditions the content of *active* chlorine decreased to about 26 per cent of the theoretical value after 300 min[41] (*Figure 4*).

In another series of experiments the irradiated polymers were isolated and the *total* chlorine content, determined by elemental analysis, was found to be about the same as before the irradiation. In the i.r. spectrum the same amide bands appeared as in the original nylon 66. This means that a photoisomerization according to the equation (18) had actually taken place.

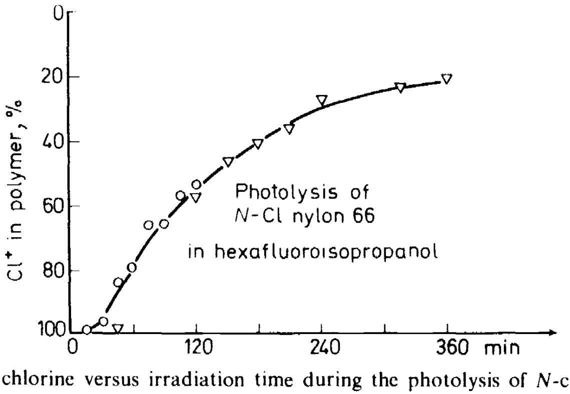


Figure 4. Active chlorine versus irradiation time during the photolysis of *N*-chloro nylon in hexafluoroisopropanol.

The position of the chlorine atoms in converted nylon is not known yet. Unfortunately no definite information can be drawn from the n.m.r. spectra. We therefore completely hydrolysed the converted nylon and about 80 per cent of the theoretical amount of adipic acid was isolated. The amine fraction was separated by thin layer chromatography into at least five compoments which have not yet been identified. This result shows that during the photo-rearrangement of *N*-chloro nylon the chlorine is mainly shifted into the amino part but a mixture of products is formed.

Since the amide group is regenerated during the photo-rearrangement and therefore H-bonds are formed again, the solubility properties of the polymer change drastically during irradiation. This change is so distinct that it can serve as a sensitive criterion for the photo-rearrangement. If, for example, we irradiate a pure solution of *N*-chloro nylon in benzene for ten minutes with monochromatic light between 405 mμ and 578 mμ no change takes place. At 365 mμ, 313 mμ and 254 mμ the solution gets turbid after a few minutes and the major part of the polymer precipitates. This means that only u.v. light below 400 mμ is active. However, kinetic or photochemical experiments are very difficult because of the great change of the solubility and the undefined large number of reaction products. The basic mechanism has therefore to be studied more extensively with low-molecular model compounds before conclusions for polymer systems are feasible.

We have carried out the photo-rearrangement in the presence of radically polymerizable monomers in order to detect the existence of radical intermediates. In the presence of styrene or acrylonitrile, a polymerization takes place, whereas in blank experiments without *N*-chloro nylon no polymerization occurs. The products obtained with styrene were crosslinked, gel-like substances and it has not been ascertained whether there is a graft copolymer or not. The product with acrylonitrile was a white solid, which could be separated into an acrylonitrile homopolymer and a fraction of a probable acrylonitrile nylon graft copolymer.

It is very interesting that the photo-rearrangement of *N*-chloro nylon also takes place in the solid state—even faster than in solution. This process can easily be demonstrated in the i.r. spectrum. We prepared a thin film of *N*-chloro nylon on rocksalt plates and recorded the spectrum. There were no NH-bands between 3300 and 3080 cm^{-1} and the amide-II-band at 1530 cm^{-1} was completely missing. Even after a longer i.r. irradiation the spectrum did not change. But when we irradiated the film with a mercury lamp for some seconds, the typical amide bands appeared[42]. After only five minutes we obtained an i.r. spectrum which was quite similar to that of the original nylon.

As the *N*-chloroamide groups disappeared during the rearrangement, the irradiated products lost their ability to oxidize, i.e. no iodine was formed from potassium iodide. This fact can be the basis for an image-forming process. If an *N*-chloro nylon film, for example, is irradiated through a negative and is dipped into an aqueous solution of potassium iodide, iodine is formed by the *N*-chloroamide groups in unexposed sites. The iodine is bound to the nylon by adsorption and therefore these unexposed parts are coloured deep brown to black. The exposed parts cannot oxidize, consequently they do not form any iodine and remain colourless.

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