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Recent Developments in Polymeric Charge Transfer Complexes

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ABSTRACT

The recent literature on polymeric charge transfer complexes is reviewed with emphasis on the author's own work. After a definition of the area and a survey of investigations on the spatial arrangement of donor and acceptor sites in the solid state, a variety of applications of these complexes is presented. Electrically conductive polymers are excluded. These applications are: compatibilization of polymer blends, liquid crystalline supramolecular organization, new developments in photoconductivity, electroluminescence, nonlinear optical properties, photorefractivity and reversible optical storage.

KEYWORDS: Polymer, Charge transfer complexes, Molecular geometry, Supramolecular organization, electro-optic applications

INTRODUCTION

Polymeric charge transfer complexes form an area of research that is fairly poorly defined and delimited. However, there is a tremendous research effort currently dedicated to polymeric charge transfer complexes, a significant part of which originates with industrial laboratories in pursuit of novel high-tech polymeric materials for a variety of applications. Most of the reviews currently available cover one or another aspect of this subject and – to my knowledge – there is no review that is trying to look at the overall research and consider each aspect as a part of a whole.

This is the task I am attempting to accomplish in the present review. I will try to mention most of the current work that falls under the general topic of polymeric charge transfer complexes. Some of these areas are huge and well reviewed previously, so I will not present any details at all. For example,

although electrically conductive polymers are definitely a very important part of polymeric charge transfer complexes, they will be covered only to the extent that they are being studied for some other useful properties (electroluminescence, third-order nonlinear optical properties). The research in polymer electrical conductivity will not be covered. I will then mention significant work previously published and emphasize the most recent scientific and technological developments. Finally, I will cover in some detail a few aspects of charge transfer interacting studies in polymers performed in my laboratory, i.e. studies of the geometry of charge transfer complexes by solid-state NMR, some aspects of self-organization and potential applications in reversible optical storage and waveguide materials.

DEFINITIONS AND PREVIOUS REVIEWS

A charge transfer complex (CTC) consists of a "mixture" of an electron donating (D) moiety with an electron accepting (A) moiety. There must be some interaction of the orbitals of the two moieties, though the extent of this interaction may vary significantly. The two moieties can belong to the same molecule (intramolecular CTC) or to two different molecules (intermolecular CTC). The orbitals' interaction usually requires a spatial proximity of the two moieties, and in this respect the intra- and intermolecular complexes may not be that different. Intramolecular CTCs are known to form by appropriately bending a molecule to allow interaction between the electron-donor and the electron-acceptor parts [1]. Probably the most important consequence of the CTC formation in "mixtures" of electron-donors with electron-acceptors is (photoinduced) electron transfer. This phenomenon is the basis for a series of potential applications: electrical conductivity (which will not be covered in this review),

photoconductivity, electroluminescence, photorefractivity and its applications in information storage and optoelectronics, etc. All these applications require a charge generation step (usually the photoinduced electron transfer) followed by a charge transport or a charge separation step. In this second step, impurities (charge traps) play a very important role, as does the tendency of the separated charges to be stabilized in their environments.

The steps leading to charge separation are summarized in a recent paper [2]. They are:
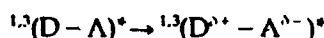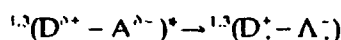
Step 1: excitation of the electron donor:

$$D + A \rightarrow {}^{1,3}D^* + A$$
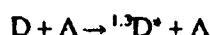
Step 2: excitation delocalized on the charge transfer complex:

$$ {}^{1,3}D^* + A \rightarrow {}^{1,3}(D - A)^* $$
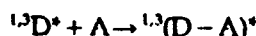
Step 3: charge transfer:

$$ {}^{1,3}(D - A)^* \rightarrow {}^{1,3}(D^{\delta+} - A^{\delta-})^* $$

Step 4: formation of the ion radical pair:

$$ {}^{1,3}(D^{\delta+} - A^{\delta-})^* \rightarrow {}^{1,3}(D_+^. - A_-^.) $$

Step 5: charge separation:

$$ {}^{1,3}(D_+^. - A_-^.) \rightarrow D_+^. + A_-^. $$
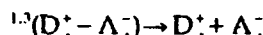
In these equations, 1 and 3 denote singlet and triplet excited states.

There is a huge amount of research involving charge transfer complexes and photoinduced electron transfer. This is in part reflected by the existence of a National Science Foundation Center for Photoinduced Charge Transfer at the University of Rochester, involving academic and industrial researchers. The most recent Nobel laureate in chemistry, R. A. Marcus, has also been recognized for his contributions in this field. Some of this research uses polymers, but a clear, separated area of polymeric charge transfer complexes does not really exist. Electrically conducting polymers, a subject of intensive research, will not be included in this review, even though the phenomena related to electrical conduction clearly involve the existence of charge transfer complexation in ground and excited states. This is because electrically conducting polymers is a subject in its own, with many pertinent reviews; hundreds of research articles appearing every month and a whole journal (*Synthetic Metals*) dedicated to organic conductors.

Polymeric charge transfer complexes require a polymer structure containing or associated with electron-donor and electron-acceptor groups. Scheme 1 illustrates some possible polymeric complexes. The literature up to 1988 covering polymeric donors mixed with acceptors, polymeric acceptors mixed with donors, blends of polymeric donors and polymeric acceptors, as well as copolymers containing
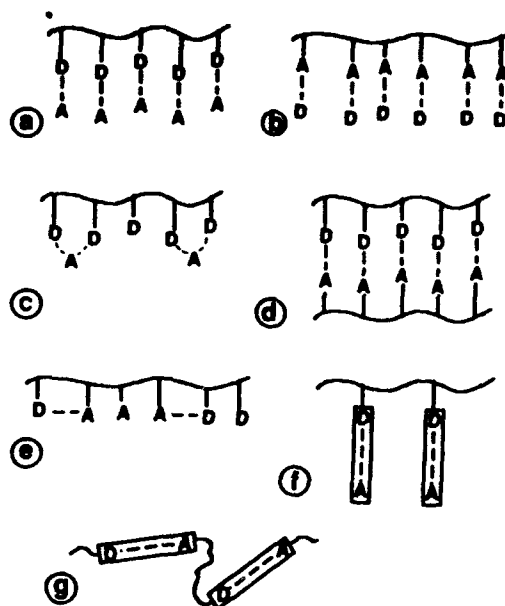
SCHEME 1.

donor and acceptor groups was recently reviewed [3]. That review emphasized mainly some synthetic and some thermodynamic aspects of polymeric CTCs.

A very important factor in polymeric charge transfer interactions is the degree of order in the system. Supramolecular organization, the spontaneous tendency to form ordered domains, has been identified as a crucial factor in organic conductivity by Wegner [4]. The conditions for organic conductivity were: existence of electron-donor or/and electron-acceptor groups, partial electron transfer and formation of separated stacks of electron-donor or/and electron-acceptor groups. This last condition was essential to allow the electron (or hole) to move along such a stack, as shown in Fig. 1.

While for a number of years the main emphasis of research into conductive and photoconductive polymers was finding the chemical structure that allows a relatively narrow bad gap for conduction, supramolecular organization has begun to receive the necessary attention. A recent review of applications of organized media [5] shows that the polymeric matrix usually presents a spontaneous tendency to order, and that in a variety of real-life applications ("Polaroid" lenses, Kodak's electrophotographic systems, etc.) this was one essential
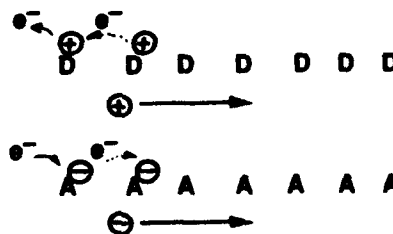
FIGURE 1. Hole transport or electron transport along two separate stacks of electron-donor and electron-acceptor groups (adapted from [4]).

property which was usually not foreseen at the time of invention. Eaton's review analyzes many systems as guest-host systems, involving some interactions, and charge transfer interactions are probably the most significant type, because they allow for photochemical applications.

More recently, Fox [6] has reviewed work performed mainly in her laboratory on electron transport. This review also recognizes the importance of supramolecular organization in designing desired properties. Supramolecular organization is not restricted to polymeric systems. Probably the most interesting development since Wegner demonstrated the necessity of supramolecular organization was a systematic analysis of liquid crystalline materials, including polymeric liquid crystals, as components of charge transfer complexes. Such studies, including the discotic phases described by Fox [6], will be briefly analyzed in this review.

THE SPATIAL RELATION BETWEEN DONOR AND ACCEPTOR: SPECTROSCOPIC STUDIES

As part of the supramolecular organization of the complexing groups, the spatial arrangement of the donor and acceptor groups within a complex will be one of the most important factors that determine the ultimate properties of the complex. It is fairly easy to investigate small molecular crystalline complexes. X-ray diffraction patterns, including single crystal analysis, correlated sometimes with solid-state NMR spectroscopy, may reveal the whole picture of the spatial arrangement of the interacting groups. Things are much more complicated when the interacting groups are part of a polymer. In most instances there is not enough crystallinity to produce a readable X-ray diffraction pattern, and the polydispersity of the polymer microstructure usually generates broadening of NMR signals because of small differences in chemical shifts. These broadened signals interfere with the relatively small chemical shifts produced by charge transfer complexation, thus obscuring any structural information.

There are very few studies in the literature investigating the charge transfer complex geometry in polymeric systems. All published studies make use of "model" systems, where the charge transfer complex is investigated in the solid state on substances similar to the structural unit of the polymer under investigation. Aromatic systems also show a definite advantage over non-aromatic ones, owing to the well-known aromatic shielding effect which may produce significant high field shifts.

Chemical Shift Effects in Solid-state NMR

Partial charge transfer from an electron-donor group to an electron-acceptor group will change the electron density, especially at the interacting sites. One would expect a decrease in electron density of the donor and an increase in electron density of the acceptor. If no other factors were present, the relevant signals of the electron-donor group should be
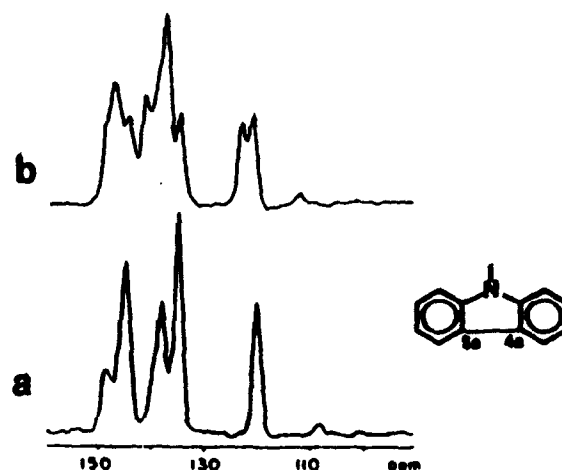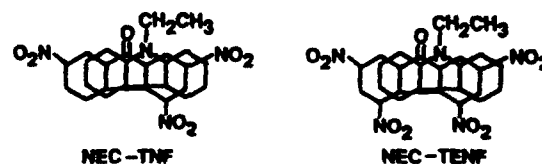

FIGURE 2. CP-MAS ^{13}C-NMR spectra of the nonprotonated carbons of the NEC–TENF (a) and NEC–TNF (b) charge transfer complexes (adapted from [7]).

shifted downfield, while the relevant signals of the electron-acceptor group should be shifted upfield. At this point, if the two components are aromatic, the aromatic shielding effect would add to the upfield shift of the carbons of the electron-accepting group and would decrease the downfield shift of the carbons of the electron-donor group. In a simple example, complexes of poly(N-vinylcarbazole) (PNVC) with 2,4,7-trinitro-9-fluorenone (TNF) and with 2,4,5,7-tetranitro-9-fluorenone (TENF), respectively, were investigated by solid-state NMR [7]. N-ethylcarbazole (NEC) was used as a "model" for the structural unit of PNVC. Figure 2 shows the spectrum of the nonprotonated carbon atoms in the two complexes: NEC–TENF (a) and NEC–TNF (b).

While it is difficult to assign every signal in the spectra, the pattern of the carbons 4a and 5a (120 ppm) shows an obvious difference between the two complexes. The two sides of the carbazole ring are identical in its complex with TENF and different in its complex with TNF. This clearly suggests a sandwich symmetrical structure for both complexes, as shown in Scheme 2.

The same information is not available in the polymer spectra, owing to significant differences in linewidths, but it is reasonable to assume that the complex geometry would be similar. Relaxation data, which will be presented in the following part of this section, support the conclusions drawn from the chemical shift data.

Another example involves a charge transfer complex between a carbazole dimer (trans-1,2-bis-9-
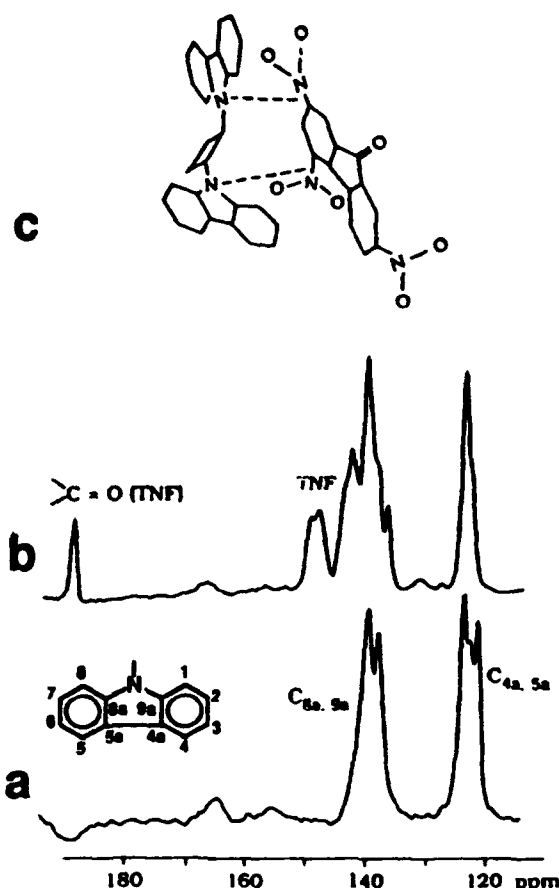

NEC–TNF   NEC–TENF

SCHEME 2.

FIGURE 3. CP-MAS ^{13}C-NMR spectra of the nonprotonated carbons of BCC (a) and a BCC-TNF complex (b). The most probable complex geometry obtained by computer minimization is also presented (c) (adapted from [8]).

carbazolylcyclobutane, BCC) and TNF [8]. The complex is also a model for a TNF complex of a polyimine containing BCC. This time, the two carbazole rings are nonequivalent in the pure dimer, but they become almost equivalent in the charge transfer complex (Fig. 3). This suggests a more symmetrical structure of the charge transfer complex, and the structure is obtained by minimization of the conformational energy of the complex using the software Polygraph. The proposed structure is included in Fig. 3.

A more interesting case which was analyzed both with models and with polymer complexes involved poly[(N-ethylcarbazol-3-yl) methyl methacrylate] (PNECMM) (its model compound was (N-ethylcarbazol-3-yl) methyl acetate – NECMAc) and poly[2-[(3,5-dinitrobenzoyl)oxy] ethyl methacrylate] (PDNBEM) (its model compound was 2-[(3,5-dinitrobenzoyl)oxy] ethyl acetate – DNBEAc) [9, 10]. The model compounds clearly show an upfield shift for both the donor and the acceptor carbons. As explained before, the acceptor's carbons' upfield shift is fully expected because of changes in electron density upon charge transfer complexation. The fact that the donor's carbons also shift upfield indicates that the aromatic shielding effect is stronger than the

electron density effect. Indeed, upfield shifts up to 5.2 ppm are observed for some acceptor carbons [9]. These are fairly large shifts. As Fig. 4 illustrates, some of the acceptor carbons and most of the donor carbons become nonequivalent in the charge transfer complex. This clearly suggests a nonsymmetrical complex geometry, in which only one of the benzene rings of the carbazole may be involved in complexation (Fig. 5).

These kind of shifts are strong enough to be noticed even in the polymer complex spectrum [10], though, obviously, line broadening is decreasing the sensitivity.

Relaxation Effects of Charge Transfer Complexation

One type of effect which is much easier to notice in the solid-state NMR spectra of the polymer complexes is a significant change in some relaxation parameters. There are many relaxation parameters which could be measured in the solid state. The carbon and proton spin-lattice relaxation time constants will be related to motions in the MHz frequency range, while the same parameters in the rotating frame will give information in the kHz frequency range. It is generally believed that segmental chain motions occur within this last frequency range, hence any $T_{1\rho H}$ and $T_{1\rho C}$ measurements could be very useful for information about this type of motion. The differences between proton and carbon relaxation are produced by their differences in abundance. Protons are abundant nuclei, their
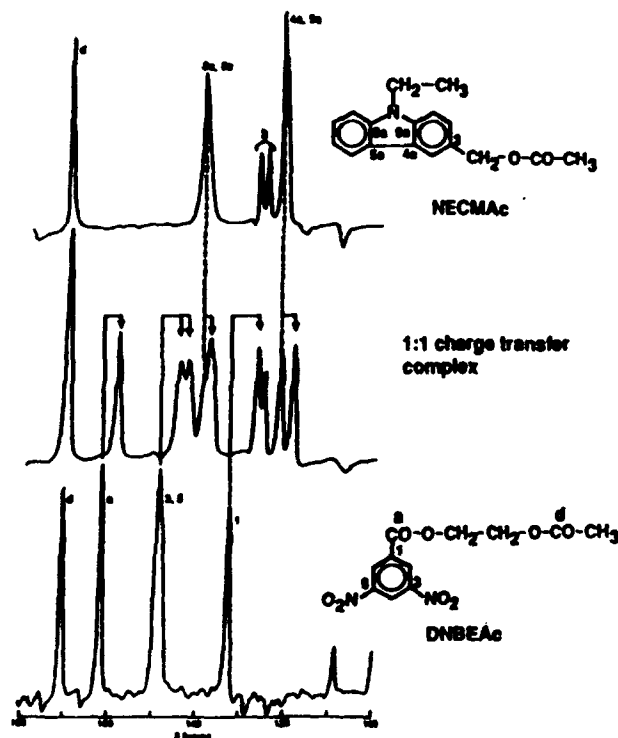

FIGURE 4. Aromatic region (nonprotonated carbons) of NECMAc, DNBEAc and a 1:1 charge transfer complex of NECMAc and DNBEAc [9].
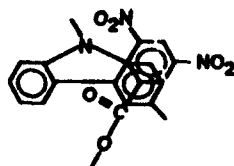
FIGURE 5. Proposed complex geometry for NECMAc and DNBEAc [9].

density is very close to the atomic density in a molecule. Carbons (isotope 13) are rare nuclei, with only about 1% of all carbons in the molecule being magnetic. That makes the density of ^{13}C very low and the probability of finding two ^{13}C atoms near each other close to zero. Hence, proton relaxation will reflect bulk properties, for example proton density in a sample, proximity of various parts of the molecule, spin diffusion within a sample, while carbon relaxation will be strictly restricted to motional influences.

It is fairly well known that $T_{1\rho H}$ measurements in polymer blends will give information about the phase structure of such blends, in the same way that the glass transition temperature (T_g) does. Phase separation acts as a barrier for spin diffusion, and spin diffusion is necessary to homogenize the $T_{1\rho H}$ values in a system with two components. Hence, if a polymer blend is compatible, a single $T_{1\rho H}$ value, usually intermediate between the components' values, will be found for the blend. Blends with interacting components usually show a positive deviation of the T_g value of the blend as compared with the additive value of the two components. This excess energy required to change the blend to its elastic state is believed to come from the nonbonding interaction (charge transfer interactions are such nonbonding interactions). Because of these interactions, the free volume available to the polymer will be reduced, hence the T_g will increase. We have demonstrated that in charge transfer interacting copolymers and blends, the $T_{1\rho H}$ values are *depressed* in a similar way to which the T_g values are increased [9-13]. An example is illustrated in Fig. 6 and
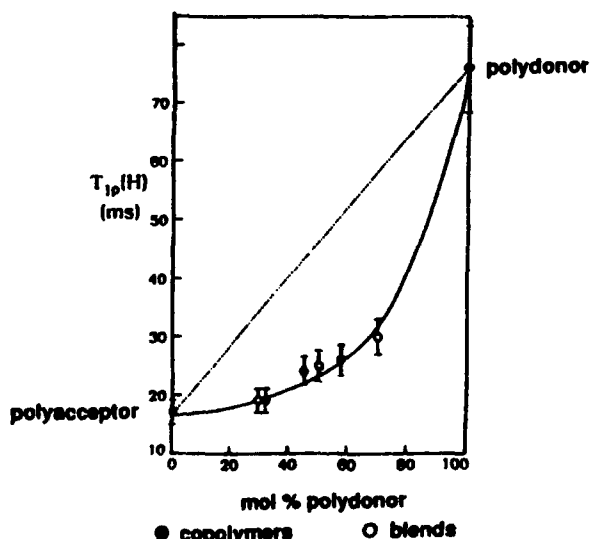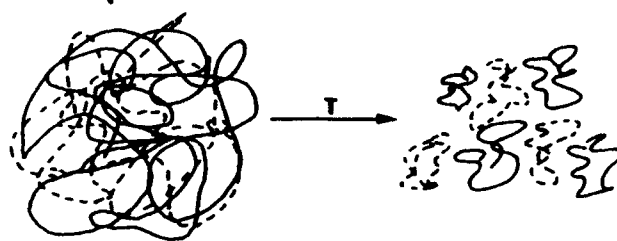

SCHEME 3.

involves both intra- and intermolecular charge transfer complexes. The polymer blends only interact intramolecularly, while the copolymers also have interacting groups on the same chain. The effect on the $T_{1\rho H}$ value seems to be similar [13].

While the copolymers are relatively unaffected by thermal treatment, the blends containing the polydonor and the polyacceptor have a lower critical solution temperature, i.e. when heated they will phase separate into the two components. Upon cooling the two components remain phase separated, as illustrated in Scheme 3.

The charge transfer interacting groups are still present throughout each phase, but after phase separation only the interacting groups situated at the interface between the two phases can reform charge transfer complexes. The consequence on the $T_{1\rho H}$ values of the system is illustrated in Fig. 7. In a blend of the two separate components in which there is no "communication" between the two phases (no charge transfer interaction at the interface), one would expect to measure two $T_{1\rho H}$ values equal to the $T_{1\rho H}$ values of the two components. If there is "communication", i.e. if some of the charge transfer

FIGURE 6. $T_{1\rho H}$ values for two homopolymers, their copolymers and their blends as a function of composition [13].

● copolymers ○ blends

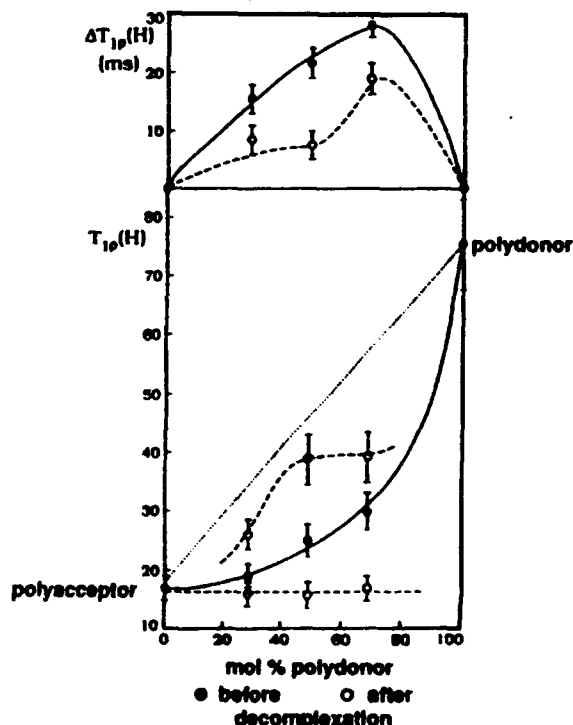**FIGURE 7.** $T_{1\rho H}$ for the compatible blends shown in Fig. 6 before and after phase separation. $\Delta T_{1\rho H}$ for both systems is illustrated at the top of the figure [13].
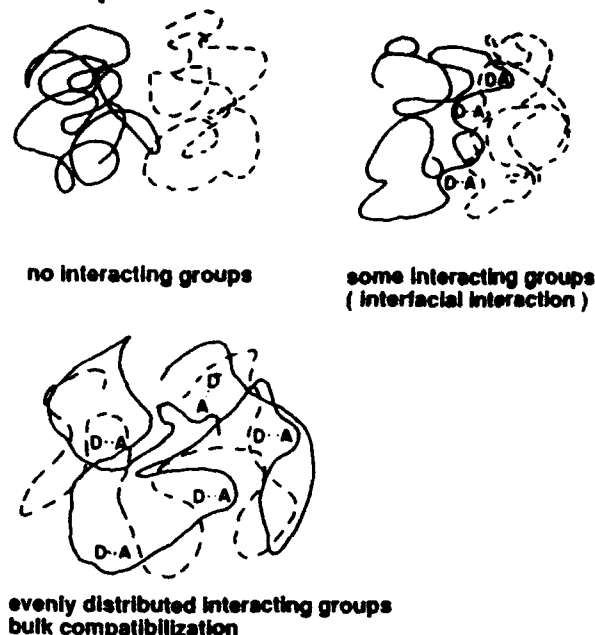
● before ○ after decomplexation

groups are interacting at the interface, then the slower relaxing component will get some help in its relaxation by the faster relaxing component through the interacting interface. Hence, for the phase separated blends, the two $T_{1\rho H}$ values measured should be one identical to that of the faster relaxing component and the other *lower* than the value for the slower relaxing component. The depression of the slower relaxing component should reflect interaction at the interface. This is indeed what happens for the system analyzed in Fig. 7. The smaller $T_{1\rho H}$ value (that of the polyacceptor) remains unaffected, while the higher $T_{1\rho H}$ value is clearly depressed in comparison with the pure homopolymer. An illustration of the depression of $T_{1\rho H}$ values as a function of composition for the compatible and for the phase separated blends is given at the top of Fig. 7. As expected, there is more charge transfer interaction within a compatible blend, because the groups are distributed and interact throughout the volume of the sample. After phase separation, there still is some significant charge transfer interaction, which now has to be localized at the interface. Though we have not attempted any quantitative analysis of the above data, it seems obvious that a correlation of the degree of interaction before and after phase separation should be indicative of the size of the phases.

One question which must be answered before $T_{1\rho H}$ starts being commonly used as a parameter indicating nonbonding interactions is to what extent does motion play a role in these changes of $T_{1\rho H}$ values? The proton spin-lattice relaxation in the rotating frame must be affected by changes in motion in the kHz range, and all the above discussion assumed that the changes in $T_{1\rho H}$ are only a consequence of the decreased free volume brought about by charge transfer interactions. The decreased free volume produces an increased proton density and hence accelerates spin diffusion (relaxation). What is the motional role? A separate study has been performed on these systems measuring $T_{1\rho C}$ as a function of temperature. This parameter is unaffected by proton density. $T_{1\rho C}$ changes very little in homopolymers, copolymers and compatible or phase separated blends when measured at similar temperatures [10]. Hence, mixing the components, allowing for charge transfer interaction, does indeed change the proton density but has little effect on the characteristic motion of the polymer molecules. This means that – at least in this case – $T_{1\rho H}$ can be used as a parameter reflecting nonbonding interactions only.

There are some other examples in the literature which show that $T_{1\rho H}$ values become depressed when charge transfer interactions are present. Complexes of PNVC with both TNF and TENF show multiple relaxation behavior, due to the inhomogeneity of the material, but the $T_{1\rho H}$ value of PNVC is always significantly depressed in its complexes [7, 14].

Scanning Tunneling Microscopy and Atomic Force Microscopy

Scanning tunneling may be proven as a very powerful method to analyze the spatial relation between

no interacting groups

some interacting groups (interfacial interaction)

evenly distributed interacting groups bulk compatibilization

SCHEME 4.

the electron donor and electron acceptor in the charge transfer complex. When properly used, this method generates pictures which can be interpreted in terms of atoms arranged in specific patterns within molecules and/or larger phases. There are very few studies published using this method to investigate charge transfer complexes, and all such studies are restricted to small molecular complexes [15–17], but it seems that polymeric complexes cannot possibly be far behind.

COMPATIBILIZATION OF POLYMER BLENDS

Directly related to the analysis of polydonor–polyacceptor blends described above are a series of studies from a few laboratories in which charge transfer complexes are being used as the driving force for compatibilization. There is a huge amount of literature concerning polymer blends and their phase structure. From a thermodynamic point of view, polymers tend not to mix together unless the enthalpic factor is dominant. Various kinds of interactions can produce the necessary negative heat of mixing to induce a thermodynamic tendency to mix. Scheme 4 shows the effect of evenly distributed interacting groups on the miscibility of two polymers.

Charge transfer interactions are obviously suitable for such a task, but they also have a few disadvantages: it is fairly complicated to synthesize appropriate groups and to introduce them on the polymer to be mixed. Then, after all this synthetic effort has been made, the results in terms of compatibilization are fairly poor. For example, one needs an average of 25 mol% interacting groups on each polymer chain to obtain a blend with a single glass transition temperature, while 5 mol% ionic interacting groups are enough to achieve the same task (at the same time ionic groups are synthetically easier to

introduce). Hence, charge transfer compatibilization is not a technical answer to a problem, but should rather be regarded as an interesting basic problem which brings with it some new insights into blend behaviour. An example of such a study is included in this issue [18]. Most of the previous studies of blend compatibilization through charge transfer interactions have involved a carbazole as donor and a 3,5-dinitrobenzoate as acceptor [19–24]. More recently, using the same donor-acceptor pair, Setz and Schneider [25] obtained very interesting information about the stoichiometry and the geometry of the charge transfer complexes where the backbone was a polysiloxane.

## LIQUID CRYSTALLINE SUPRAMOLECULAR ORGANIZATION

Among the possible types of order in polymeric systems, liquid crystalline order allows a variety of potential arrangements and is less restrictive than crystalline order. There are no examples of crystalline polymers with charge transfer interactions, although there was a lot of speculation about the kind of order in solid PNVC. It is now accepted that the carbazole rings are arranged in a manner that allows hole transport, i.e. fairly regularly among the polymer chains [26]. This arrangement is similar to a lowly ordered nematic phase, but there is no evidence that such a phase exists in PNVC. A depressed nematic phase was postulated for complexes of 1,4-bis[2-(4′,4″-dialkoxyaryl)ethynyl]benzene derivatives with p-chloranil [27]. These are just models for polymeric complexes. A decomplexation was postulated as the mechanism for complex decomposition. Further studies on nematic phases of polymers involving p-chloranil as the acceptor molecule [8] seem to indicate that nematic phases are produced only in the presence of residual solvent, and that decomplexation involving a small molecule, as opposed to a polymer, is unlikely to generate an endothermic peak in the DSC trace.

By far the most interesting work in this area is that on, columnar discotic phases formed with electron-donors, electron-acceptors or combination of these. Some of this work does not involve chemically bonded discotic mesogens, i.e. these are polymers only because there is a physical long range order. These compounds show a tremendous potential for charge migration and all the applications that may be derived from this phenomenon [28]. In this example, the discotic mesogen is a substituted porphyrin which forms tilted columnar stacks. As early as 1989, it has been demonstrated that liquid crystalline columnar phases can be induced by charge transfer complexation in amorphous polymeric systems. A few examples of the components are shown in Scheme 5.

Typically, the complex consists of an amorphous polymer containing electron-donor groups based on triphenylene either on the side chain or in the main chain. The acceptor is TNF, as it is usually added as a dopant to the polymer. The charge transfer complex shows liquid crystalline phases which are schematically represented in Fig. 8 [29].

A very interesting point was that TNF could serve as a "compatibilizer" when two of those amorphous polydonors did not mix. A discotic mesophase was formed only when TNF was added and a single phase with three components (two of them polymeric) was thus obtained. Such complexes were investigated for a variety of compositions and their phase diagram was established [30]. The procedure to induce columnar mesophases works also when TNF is incorporated into a polymer which is subsequently doped with a donor based on triphenylene [31]. Finally, an obvious consequence of these studies was to extend ordering in such systems using the Langmuir Blodgett procedure to obtain multi-layered ordered structures [32].

This area of research will probably receive much more attention in the near future, as it becomes clearer that supramolecular organization is one of the main factors affecting the overall properties of a particular material.

POLYDONORS

TNF (acceptor)
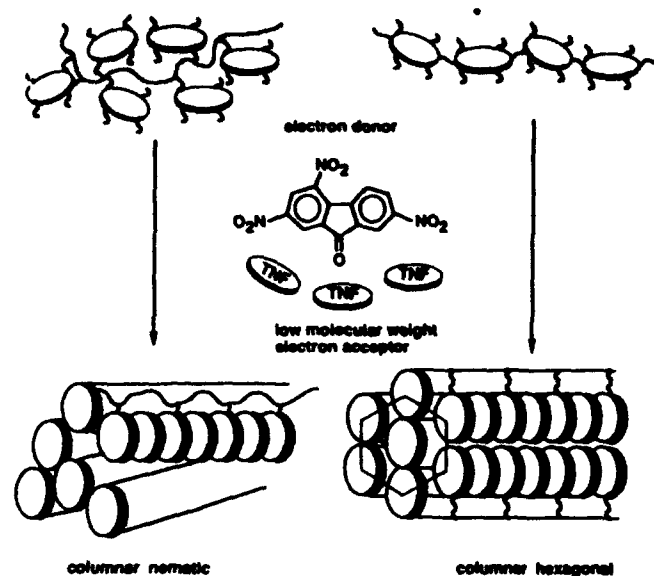
POLYACCEPTOR
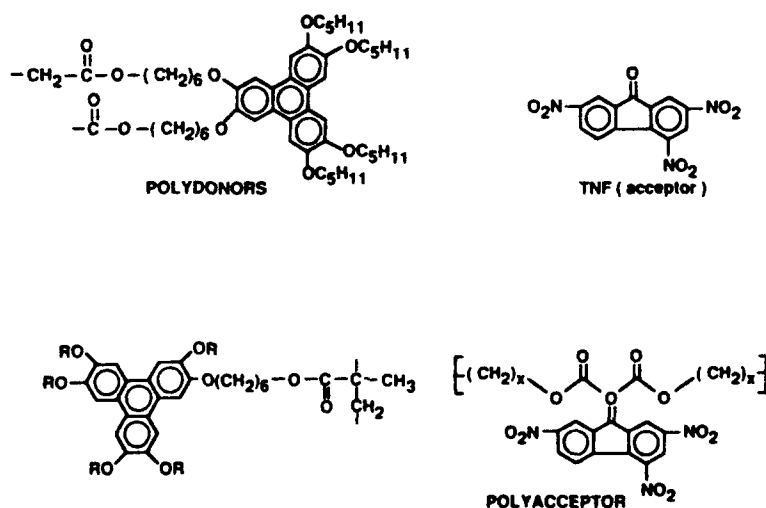
SCHEME 5.

FIGURE 8. Induction of discotic phases in amorphous electron-donor containing polymers [29].

ELECTROLUMINESCENCE

A recent review on polymeric materials which could be used in electroluminescent devices is a very useful reference for anyone interested in the subject [33]. It covers most of the work in a field that started with a publication in *Nature* in 1990 [34]. The advantage of polymers in electroluminescent displays is mainly related to their unique processing abilities, allowing large display surfaces with minimal production costs. Electroluminescence is a result of dual charge injections which travel towards each other across a polymer film and combine to form an exciton. The charges are injected through an electric field in the electrodes deposited on the top and bottom of the polymer film. Hence, charge transport of both types (electrons and holes) is a crucial property for the polymer film. Conjugated polymers such as poly-(phenylene vinylene) (PPV) and analogous structures (Scheme 6) have been found to be ideal for electroluminescent devices. PPV is insoluble, hence its synthesis as films for devices has constituted a challenge for years. Now, the precursor synthesis of PPV is very well known and broadly used [33].

There are two main types of problems related to such devices. One is of a physical nature and involves research into electrode type and deposition, charge injection, charge transport, efficiencies, etc. The other type of problem is of a chemical nature and involves selection of polymeric materials which could create various colors (the color of the emitted light is obviously related to the band gap of the polymer used) and devices of various flexibility [35]. The most intense subject of research recently seems to be the search for blue light emitting polymers.
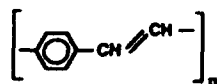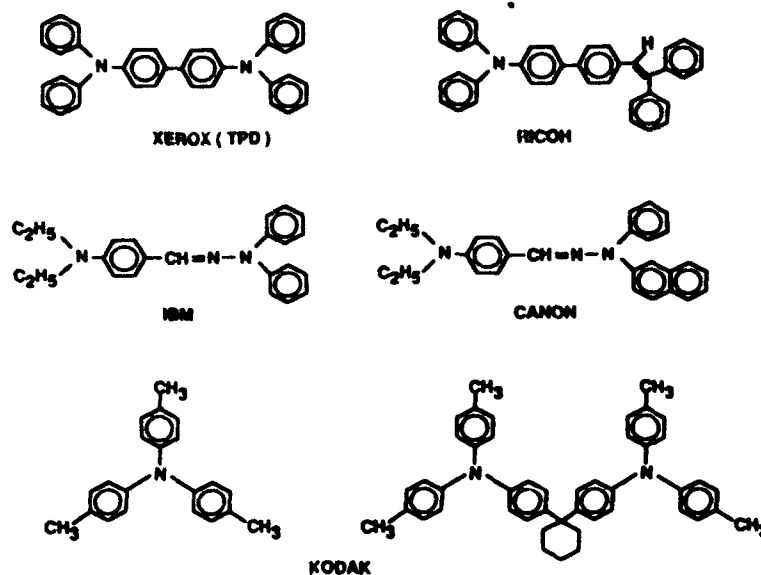

SCHEME 6.

Highly conjugated PPV emits yellow light, thus, in order to increase the band gap and create blue luminescence, various synthetic methods are proposed to create interruptions in conjugation [36, 37]. Not surprisingly, supramolecular order has been proven to affect the efficiency and the band gap of such electroluminescent devices. Pre-ordering PPV in the preliminary synthesis significantly changes these parameters [38].

NEW DEVELOPMENTS IN PHOTOCONDUCTIVITY

The main drive for research in photoconductive polymers comes from the applications in electrophotography and laser printing. The photoconductive material in a typical copying machine is composed of two layers: one which photogenerates the charge (electron or hole) and the other which transports the charge towards an electrostatically charged surface. The whole process and a recent review of organic photoconductive (for the generation layer) compounds was published recently [39]. That review also covered significant aspects of the charge transfer interactions occurring in these materials and their significance for the charge generation processes. Laser printing applications use the same compounds as those used in the generation layer in electrophotography. We will briefly describe in this section relevant aspects of designing the charge transport layer.

The charge transport layer is usually composed of an active substance, typically an electron-donor compound for hole transport, dispersed in an "inert" matrix. Scheme 7 shows the electron-donor compounds used by various companies. The matrix is normally a transparent polymer film which can accommodate a significant amount of active substance dissolved into it. It has been demonstrated that charge mobility is directly proportional to the concentration of the electron-donor. Until recently it

SCHEME 7.

was believed that the matrix was inert, but now it becomes increasingly clear that there are some sort of weak interactions between the active compound and the matrix that affect charge mobility. This has been demonstrated mainly by comparing a polycarbonate with a polystyrene matrix [40–42]. The higher mobility in the polystyrene matrix is assigned to the absence of dipolar fields generated by the polar groups in polycarbonate. Polar impurities are also shown to decrease the desirable properties of the materials. My recent studies by solid-state NMR on charge transport materials based on polycarbonate were performed based on the same principle described in the section about the charge transfer complex geometry. $T_{1/H}$ values were measured for the polycarbonate and for the materials containing increasing amounts of TPD. If no interaction (dipolar, charge transfer or any other type) takes place in the material, one would expect a linear increase of $T_{1/H}$ values with the increase of the TPD content. What happens instead is that $T_{1/H}$ values decrease initially, suggesting increased proton density, based on the arguments presented earlier. This is in agreement with the existence of some sort of interaction between the matrix and the active compound [43].

Another very interesting area of research is investigation of electron transport materials. As a general rule, they should be electron-accepting compounds dispersed into an "inert" matrix (again, a nonpolar matrix should be favorable for increased mobility). Such compounds are usually less soluble in commercial polymers, though the solubility increases with the polarity of the matrix. The mechanism of charge transport has been presented previously in fig. 1. Electron donor compounds act as hole transport materials. The ionized electron donor is now an electron-deficient molecule and will accept an electron from another electron donor group situated immediately next to it. Hence, the ionized donor is actually playing the role of an electron-acceptor in a charge transfer relation. This is the

reason why there is no need for the whole electron-donor electron-acceptor pair in a charge transport material. The electron transport along an electron-acceptor stack, also described in Fig. 1, functions on the same principle: the ionized electron acceptor is now electron-rich and can act as a donor to the next electron acceptor molecule in the stack. One of the most interesting classes of compounds investigated is unsymmetrical dibenzoquinones of the general formula presented in Fig. 9 [44].

NONLINEAR OPTICAL PROPERTIES

A fairly recent review of materials with nonlinear optical properties and their possible uses includes examples of organic and polymeric materials [45]. The research in this area is extensive and centered mainly around second- and third-order materials. A good introduction and survey of the literature is given in reference [46]. I have decided against trying to provide an update of the literature in this chapter. The amount of publications is outstanding and any attempt to review it becomes obsolete in a few weeks.

Second-order nonlinear materials show a significant second-order susceptibility, and in organic and polymeric materials this is based on the existence of parts of the molecule which may be preferentially oriented to create a bulk susceptibility. Typically, a mesogenic structure of the type shown in Scheme 1 (f or g) is required. Noncentrosymmetry is absolutely necessary for such a group. It consists of a fairly rigid conjugated or aromatic skeleton with an electron-
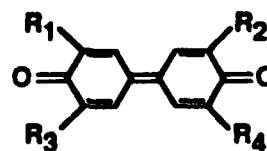

FIGURE 9. General structure of a dibenzoquinone [44].

donor group at one of the ends and an electron-acceptor group at the other. Owing to the presence of the π-electrons, such a structure will have a permanent polarization dictated by the ionization potential of the electron donor and the electron affinity of the electron acceptor. Such a structure can be dispersed into a polymer to function as a guest-host system, or can be attached within a polymeric structure by spacers long enough to allow the necessary parallel orientation which confers second-order susceptibility.

The bulk second-order susceptibility is only obtained when most of the mesogens are oriented parallel with the donor groups pointed in the same direction. This is usually achieved by a process named "poling". The polymer film is sandwiched between two electrodes and a strong electric field is applied while the film is heated above the glass transition temperature. The mesogenic groups will then tend to organize in the same direction, with the electron-acceptor groups pointing toward the positive electrode and the electron-donor groups pointing toward the negative electrode. After maintaining the film above T_g to allow an equilibrium to be reached, the film is then slowly cooled with the electric field on. This "freezes" the orientation of the mesogens and if room temperature is much lower than T_g, produces a relatively stable material with second-order susceptibility. It is worth mentioning that liquid crystalline properties are not a requirement in order to pole such a material, hence the term "mesogen" is only used here by analogy with the liquid crystal use. The best known property of materials with second-order susceptibilities is second harmonic generation, where the output wave has twice the frequency of an input wave in a device.

One potential problem of such materials is lack of long term stability. Even when the operating temperature is much lower than T_g, the orientation is slowly being lost over a long time. There are many recent studies that make use of crosslinking or magnetic prealignment or even prealignment before polymerization and thus produce materials with improved stability.

Third-order materials have no symmetry requirements. As with the second-order materials, polymers are just one class of such materials, the newest ones to attract attention from this point of view. Polymers with significant third-order susceptibilities are typically those that also have the ability to conduct electricity, but polymers with heterocyclic ladder-type structures are also very good. One of the papers published in this issue deals in detail with third-order susceptibilities [47].
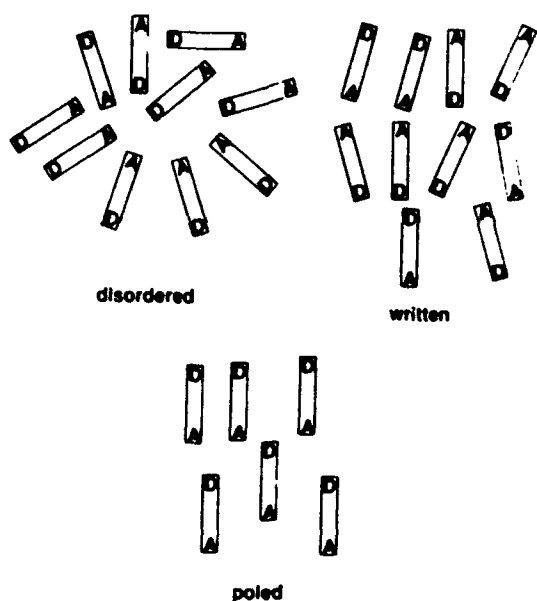
PHOTOREFRACTIVE POLYMERS

Photorefractivity is a phenomenon that was noticed initially in inorganic materials and its consequences are a series of very exciting optical properties which may lead to a variety of uses, the most important being holographic storage. Photorefractive polymer materials have been proposed only very recently [48, 49]. They are usually materials which are both

photoconductive and show second-order nonlinear optical properties. To show both properties, the materials are designed as host-guest systems. One could start from a photoconductive polymer (which is usually a mixture of a polymer matrix and a charge transport dopant) and add another guest molecule with second-order susceptibility. Or one could start with a second-order nonlinear polymer (in which the active sites could actually be chemically bonded to the main chain) and dope it with a charge transport substance. Either way, in order to assure the presence of the second-order nonlinear optical properties, the material has to be poled in strong electric fields, as was described in the previous section. The steps necessary to achieve photorefraction are: charge generation, transport, separation (trapping) and the electro-optic effect [50]. This last term means that the refractive index of the material will depend on the intensity of the electric field generated in this case by the separated charges. Recently, novel photorefractive polymers have been proposed which incorporate all the active components within the polymer structure [51-52]. Note that for a polymer to be really photorefractive, the electro-optic effect has to originate with the charge separation given by the previous steps and not with some other phenomenon. For this reason, photochromic groups are usually avoided in the preparation of photorefractive polymers.

REVERSIBLE OPTICAL STORAGE

Since the commercial success of the optical compact disk, a great variety of materials and methods has been proposed for reversible optical storage. The compact disk is a memory storage of the type Write Once Read Many times. The commercial reversible storage devices are based on magnetic or magneto-optic principles. Owing to the great interest in photonics (the optical equivalent of electronics) and its applications in optical switching, waveguides, optical computers, real-time holography, etc. [53], a great variety of potential systems for reversible optical storage has been proposed in the scientific literature. The principles on which the optical storage process is based are very different at times; however, a series of such processes is based on various photochromic effects. A recent book [54] reviewed some of the potential applications of a few photochromic polymeric materials.

We will describe in this section one reversible optical storage system which is a combination of a liquid crystalline, nonlinear optical and photochromic effects. This system was first proposed by Todorov *et al.* in 1984 [55], rediscovered in 1987 as a liquid crystal polymer phenomenon [56], and again re-evaluated as a more general, locally erasable medium in 1992 [57]. The materials are polymers containing aromatic azo groups (usually substituted azobenzenes) which undergo photochemical *trans-cis* isomerization. In this respect, the phenomenon could be considered photochromic, although the typical azobenzenes used have electron-donor and electron-acceptor groups in the *para* position, and
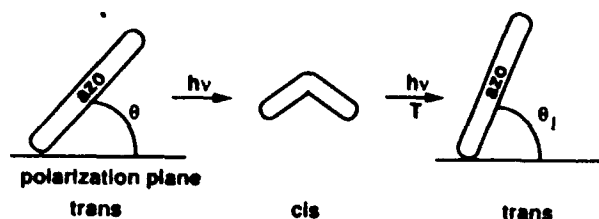
disordered

written

poled

SCHEME 8.

polarization plane

trans   cis   trans

FIGURE 10. Scheme of *trans-cis-trans* isomerization of an azobenzene group.

the absorbances of the *trans* and *cis* forms are not that different [58]. Hence, a *trans-to-cis* change will not produce a change in color, as photochromic substances show. Moreover, the *cis* form in such substituted azobenzene has a lifetime of the order of milliseconds to seconds. At equilibrium there is no *cis* isomer left in the polymer. The way to encode a bit on such polymer film is not based on the photochemical configuration change, but on an overall orientation of the azobenzene groups parallel to a preferred direction. In this respect, the phenomenon could be considered a liquid crystalline effect, in that order is being induced into an otherwise amorphous, random system.

Although this phenomenon was extensively studied in liquid crystalline polymers, and information was being stored by changing the alignment in a preoriented sample to another direction in the part subjected to light, one cannot really characterize the oriented part in an otherwise amorphous polymer as liquid crystalline. Finally, from a nonlinear optical phenomenon point of view, the *trans* azobenzene groups have second-order nonlinear susceptibility when they have electron-donor and electron-acceptor substituents in the *para* positions and the organization produced by irradiation could be considered almost equivalent to a poling process. In fact, both an electric field and irradiation are necessary to achieve an orientation with all the donor groups pointing in the same direction [59], as shown in Scheme 8.

Thus, the role of the charge transfer interacting groups in this particular reversible optical storage is twofold. First, their presence shifts the absorbance of the *trans* azobenzene to higher wavelengths (lower energy required to activate the *trans-cis* isomerization process) and at the same time activates the thermal and photochemical *cis-trans* isomerization. Donor-acceptor substituted azobenzene require less energy and time to be oriented. Second, they allow formation of a "written" part which also possesses

second harmonic generation properties and has been proposed as a potential waveguide material. A review covering most of the recent azobenzene studies has been published recently [60].

The mechanism of orientation of the azobenzene groups is based on changes induced by polarized light [57]. Figure 10 illustrates schematically the *trans-cis-trans* isomerization cycle of a single azobenzene group. The *trans-cis* isomerization rate is proportional to the laser irradiation and to a term $\cos^2 \theta$, where θ is the angle between the laser polarization plane and the dipole moment of the azobenzene group. The *cis-trans* isomerization is relatively fast and is thermally or photochemically activated or both. At the end of a *trans-cis-trans* cycle, owing to significant changes in the shape of the azobenzene group, its orientation may be slightly different from the initial orientation. If the new orientation still has a component of the dipole moment in the laser polarization plane, then the azobenzene group will still be activated for a new *trans-cis-trans* cycle. If after the end of such a cycle the azobenzene group happens to fall perpendicular to the polarization plane, it will remain inert and unchanged independent of how long the laser is being kept on. In a statistical process, every azobenzene group goes through many such cycles until it falls perpendicularly to the polarization plane. The consequence is that the orientation perpendicular to the polarization plane will become enriched to the point where its population is significantly greater than the population in any other direction. this can be verified by measuring IR or UV-vis dichroism and birefringence [61].

"Writing" is achieved by a laser beam of 5 mW on a spot of 400 μm diameter in a few milliseconds. The birefringence attains a maximum value (saturation) and it remains constant as long as the writing beam is on. A typical writing beam could be an argon laser operating at 488 or 514 nm. When turning the writing beam off, there is some relaxation which diminishes the total birefringence achieved by about 20%. This may be associated with dissipation of the local heat associated with the laser beam and is a decrease of the total number of aligned azobenzene groups. After this relaxation, which takes place in a few seconds, the level of birefringence remains constant for a long time (two years were verified on our samples). The stability of this "writing" is directly related to the glass transition temperature of the polymer when the azobenzene group is bonded within the polymer structure. The higher the T_g, the better the stability at room temperature. If the azobenzenes are just dissolved as a guest-host system in

a polymer matrix, the writing is only stable for a few minutes or hours. "Erasing" can obviously be achieved by heating the polymer to or above T_g. This will allow the frozen orientation to randomize back. But a much more exciting way to erase the written orientation is by using a circularly polarized laser beam, which will produce no preferential orientation, and thus will photochemically restore disorder following the same mechanism as the writing process. This is local erasing, with the same resolution as the writing process. A typical writing–erasing–rewriting curve is shown in Fig. 11 [62].

Almost any azobenzene-containing polymer can be used as reversible optical storage. A variety of structures has been proposed by my research group and by other groups. One important factor is that the quantum yield of the *trans–cis* isomerization process has to be as high as possible and the activation energy for the same process has to be relatively low. If one introduces a chlorine atom in the ortho to the azo group (using disperse red 13 instead of disperse red 1 as precursor) [63], for example, the writing process is slowed down.

There are quite a few factors that seem to play a significant role in this reversible optical storage process. For example, the film thickness is very important, because the writing beam is being absorbed, hence its intensity varies through the film [64]. Variation of the azo groups concentrations, as in copolymers or blends, for instance, changes the writing characteristics. Probably the most important factor is the spontaneous tendency of the azo groups to form oriented domains. If an azo-containing polymer is crystalline, or liquid crystalline within a certain temperature interval, the thermodynamic tendency to form oriented domains will reinforce the action of the writing laser beam, producing higher birefringence levels [65]. However, the same tendency will run against the action of the erasing laser beam, making erasing much slower and incomplete [66]. The most interesting aspect of optical storage on crystalline and liquid crystalline polymers is cooperative orientation of any other mesogenic groups present in the structure induced by the orientation of the azobenzene groups. This enhances

the birefringence achieved on such polymers well above the possible levels in amorphous polymers.

CONCLUSIONS

This brief survey of the recent developments in polymeric charge transfer complexes is certainly incomplete, but – I hope – it gives the reader an overview of an extremely active and exciting field of research. The potential applications of the newest scientific development open new avenues for smart materials and optoelectronics. I can only hope that there will be more interaction in the future between the diversity of scientists involved in polymeric charge transfer complexes.

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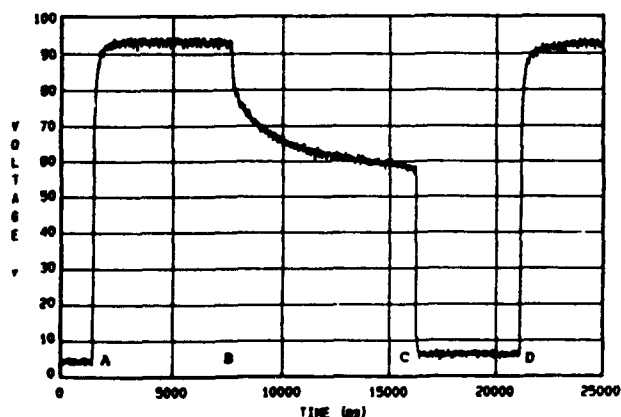26. A. Natansohn, *J. Polym. Sci.: Part A: Polym. Chem.*, 27, 4257 (1989).

FIGURE 11. Writing–erasing–rewriting curve: A, writing beam on; B, writing beam off; C, erasing beam on; D, writing beam again on [62].

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