

Polymers and Light

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Polymers and Light: Challenge and Perspectives

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Optical and photochemical properties of polymers are of importance in a number of situations including photoresist systems, nonlinear optics, photochromic systems, and photoconductor applications. Recent advances stem from new materials such as polymers prepared by ring-opening metathesis polymerization (ROMP),

conducting polymers, and redox-active polymers. Advances include new methods for duplicating the early events in natural photosynthesis, examples of novel photoconductors, and electroluminescent diodes. Relating structure and composition to function remains an important fundamental aspect of research in the area of

polymers. Some specific recent work relates to the use of ferrocene-based polymers confined to electrodes for the sustained photoelectrochemical reduction of CCl_4 ; fluorescence and energy migration following light absorption by aryl-alkyne rigid rod polymers; energy and electron transfer following light absorption by functional polymers prepared by ROMP having an ordered arrangement of chromophore and quencher(s); and demonstration of a photovoltaic device using an oligomer of polythiophene as the critical device material.

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Linear and Nonlinear Light Chromophore Interactions

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Abstract. Polymers play an important role in the field of photochemical applications and photo-electrical applications. In this article we will focus on some typical examples of using polymers in modern technologies taken from the field of photoconductivity, photochemistry, and nonlinear optical applications. The latter field points towards a new direction, namely using polymers for optoelectronic applications. It will be shown that the technical material requirements for optoelectronic applications are rather different from the requirements which have to be fulfilled for conventional photochemistry and photophysics. It will be more and more the solid-state and semiconductor aspects which will enter the field of research, and development and these new aspects will be as important as the aspects of conventional polymer physics.

Introduction

Polymers are ideally suited for applications with visible light since they are, in general, nonabsorbing in the visible range

and, due to their amorphous structure, they do not scatter light. By implementing chromophores into polymer matrices various light-induced processes can be 'tailored' to special applications such as:

- Special Photochemical Reactions in Polymers
- Light-Induced Structural Changes of Polymers
- Light-Induced Conductivity Changes of Polymers (Photoconductivity)
- Light-Driven Nonlinear Processes in Polymers
- Current-Driven Luminescence Properties of Polymers (Electroluminescence).

Along with the above photonic properties there is a whole series of applications which are based on the various photoreactions as summarized above. These applications are:

- *Photochemistry*: Photo-lithography, Printing Techniques, Photoresist Applications, Optical Memories, etc.
- *Structural Changes*: Holographic Applications, Optical Memories, etc.

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Fig. 1. Light sensitivity of various technically used materials, compared to the sensitivity of the human eye [1]

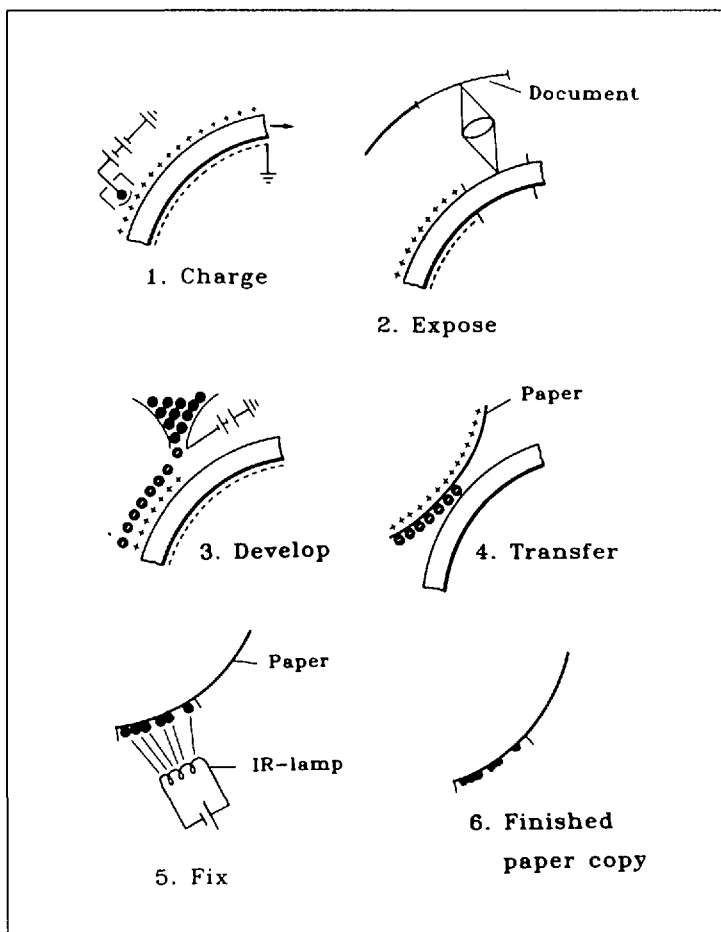
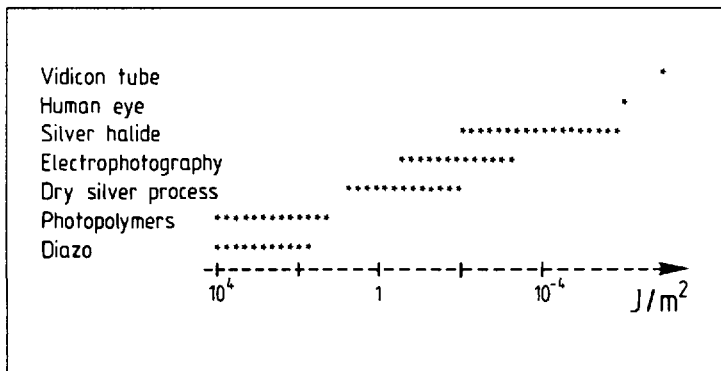


Fig. 2. Principle of the electro-photographic process: 1) corona charging (switching on the battery), 2) exposure of photoconductor, 3) development process, i.e. transfer of charge carriers through the photoconductive layer and electrostatic transfer of toner particles, 4) transfer of toner particles to the paper, 5) thermal fusion of toner particles to the paper, 6) finished paper copy (or finished offset-master)

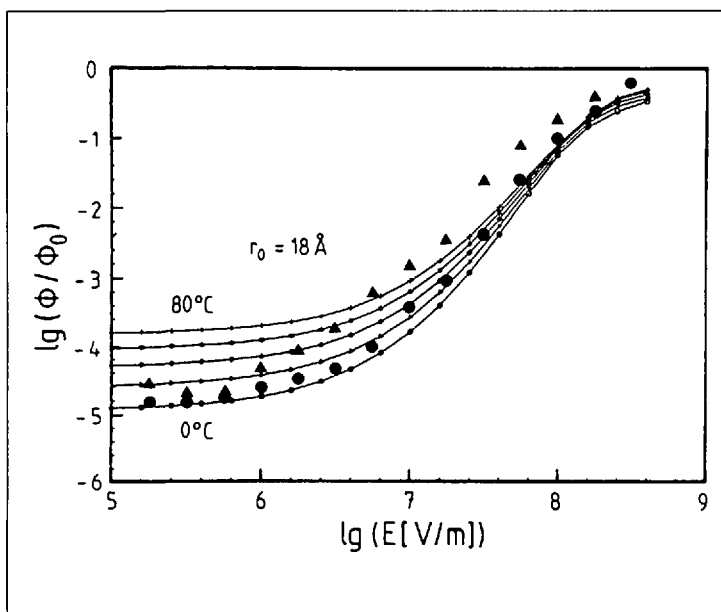


Fig. 3. Quantum yield of electron-hole separation as a function of the applied electric field (double log plot). The experimental points are taken for the polymer polyvinylcarbazole at 80° (triangles) and at 20° (circles). The calculated curves are the prediction of the Onsager theory (see [2]).

- Photoconductivity: Electrophotography (Xerography), Laser Printing, Offset-Technologies, etc.
- Nonlinear Processes: Frequency Doubling of Light, Optical Modulators, Optical Switching (Light with Light), etc.
- Electroluminescence: Display Applications, etc. (technologically this field is not yet established but has high potential).

With the multitude of applications, as mentioned above, it is obvious that photoactive polymers have penetrated most technologies and, above all, they have revolutionized the information technologies. In this contribution we cannot cover all the aspects of photonic applications of polymers. We will, however, elaborate on a few typical examples which we will select according to the degree of the light sensitivity of the various light induced processes.

1. Photoconductive Polymers

Photoconductive polymers have the highest light sensitivity; they are listed in Fig. 1 under the group 'electrophotography'; the figure gives a survey over light sensitivities of various materials. The high light sensitivity of photoconductive polymers is due to the fact that the photon triggers a reaction, the electron-hole formation, which leads to an electric current which is driven by an external battery. After the electron-hole formation the polymer changes from an insulator to a conductor and thus the battery can, as pointed out above, cause an electric current, the photocurrent, to flow through the sample. This photocurrent can be used for all kinds of imaging purposes.

The use of an external high-voltage battery in the form of a corona charging process is, therefore, the main cause for a true 'gain mechanism' which characterizes photoconductive applications as being very light-sensitive. A typical photoconductive application is shown in Fig. 2 which depicts the various mechanisms of the electrophotographic process.

It is interesting to note that the quantum yield for light-induced electron-hole separation, which is the primary photonic step of the photoconduction process, can be on the order of unity (at high applied fields) and, therefore, applications based on photoconductive polymers lead to very efficient technical applications and are the basis of a multi-million dollar industry. Fig. 3 shows the quantum yield for electron-hole separation in polyvinylcarbazole; here the carbazole substituent of the polymer chain is the photoactive group.

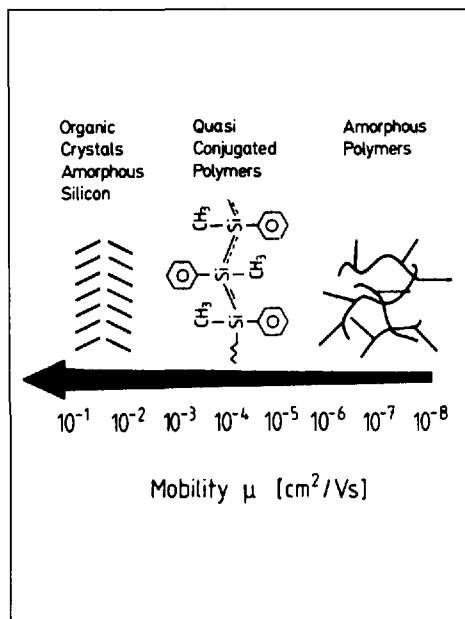


Fig. 4. Mobilities of typical organic materials

In carbazole, the photoactive state is the excited singlet state of the carbazole moiety, and this excited singlet state can be ionized in a strong external field (for a review, see [3] and quotations therein). Fig. 3 shows that the usage of very high electric fields is instrumental for a successful application of photoconductive polymers. Only at high fields can the light-induced carriers be separated with high yields (note the logarithmic scale of Fig. 3).

The limitations of presently used photoconductive polymers are the low charge carrier mobilities. These are, for amorphous media, on the order of 10^{-6} cm^2/Vs and have to be compared with the mobilities of semiconductors which are on the order of 10^0 to 10^3 cm^2/Vs and, therefore, more than 6 orders of magnitude higher. At the present time the low mobilities of polymeric materials limit the printing-speeds and process-speeds of the various technical applications.

Fig. 4 shows, symbolically, that through the use of conjugated and quasi-conjugated polymers [4][5] and through the use of more ordered structures like discotic liquid crystals [6] the mobilities of organic materials can, in principle, be increased by 3 orders of magnitude to values of *ca.* 10^{-3} cm^2/Vs . These values, however, are still smaller than the mobility values of organic single crystals which are on the order of 1 cm^2/Vs (see [3] and [7]).

Besides tailoring materials for higher mobilities the presently used photoconductors have to be sensitized towards the red spectral range for applications in conjunction with semiconductor lasers. These sensitization processes can be achieved by using organic dye and pigment systems.

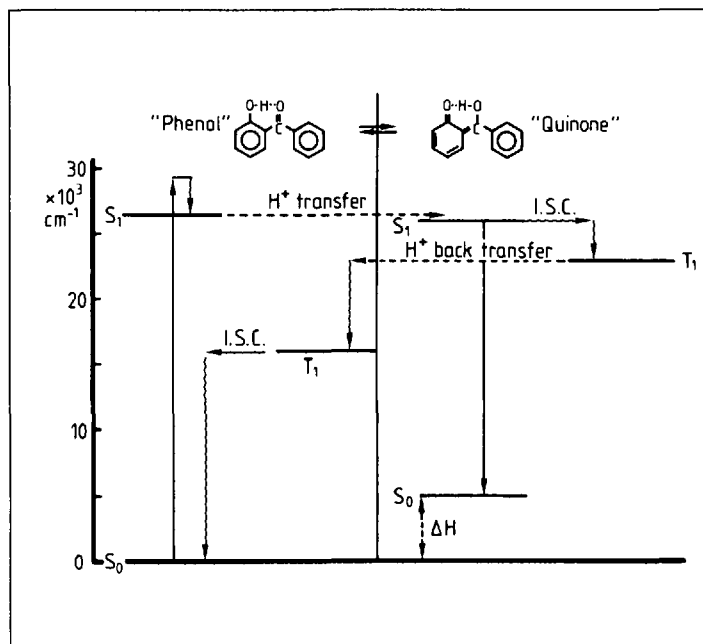


Fig. 5. Proton transfer in 2-hydroxybenzophenone [8]

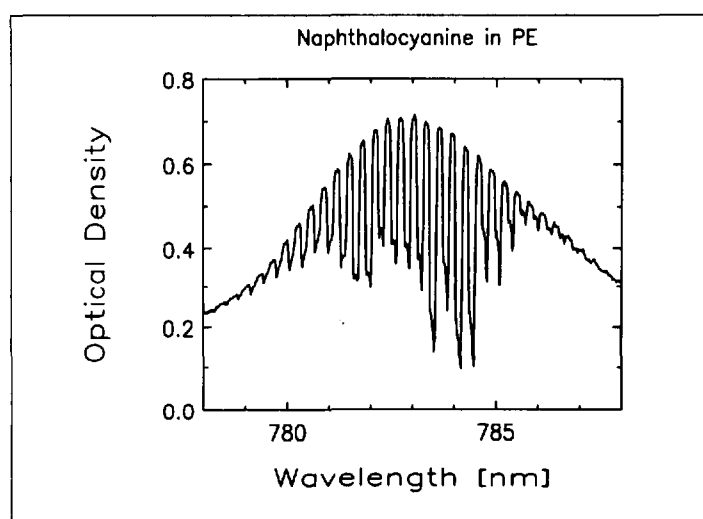


Fig. 6. Frequency-selective photochemical changes of a phthalocyanine photon-transfer system. The photoreactive molecule is naphthalocyanine doped into a polyethylene film [11].

2. Photoreactive Polymers

Photoresists applications are, as far as their sensitivity is concerned, the applications following the photoconductive applications (see Fig. 1; photopolymers). The multitude of possible photoreactions in polymers is rather large, and the reader should be referred to pertinent review articles [1].

From the physics point of view some of the most fundamental and also rather simple photochemical reactions are proton-transfer reactions. These reactions are often combined with molecular rearrangement processes such as *cis/trans*-rearrangements [8]. Many years ago one has recognized already that proton-transfer reactions can be utilized to dissipate the electronic energy of photons without causing permanent photochemical damage of the involved organic materials. In this context proton-transfer materials have been used as UV stabilizer dyes and are used as additives to many polymers [9].

Fig. 5 gives a typical and rather well investigated example of a proton transfer reaction of the molecule 2-hydroxybenzophenone. Note that the first electronic step is the excitation of a rather polar excited singlet state.

Often the proton-transfer reactions are followed by a *cis/trans*-isomerization which can lead to a stabilization of the photoproduct state. *cis/trans*-photoreactions have also lead to applications in the field of holography [10]; here the molecular *cis/trans*-reactions give rise to rather large changes of the refractive index of the involved materials. The large Δn changes can be used to prepare polymer films containing photo-active *cis/trans*-dyes which are characterized by quite high holographic refraction efficiencies (> 50%).

A rather recent photochemical application based on proton-transfer systems is the photo-induced tautomeric reaction of phthalocyanine- and porphine-like molecules.

Since in the above mentioned tauto-

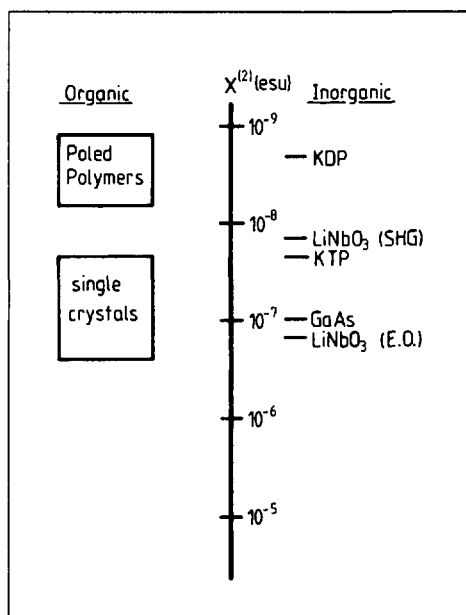


Fig. 7. Comparison of the $\chi^{(2)}$ values of organic and inorganic materials [15][16]

meric reactions the photoproduct tautomer is, from a chemical point of view, degenerate with the educt molecule, the photochemical change involves the interaction of the tautomeric molecule with the matrix environment.

These molecule-matrix interactions give rise to very small spectral changes. Going along with these small photochemical changes, however, are extremely narrow linewidths of the involved photochemical bleaching processes. Therefore, the photochemistry can be used in terms of very narrow-band and frequency-selective photochemistry and can thus be utilized for multi-frequency optical storage. In this novel storage scheme the number of frequency channels can be larger than 10^3 [11–14]. Fig. 6 shows a sequence of photochemical bleaching reactions in a phthalocyanine-type molecule embedded into a polyethylene host polymer. The photochemistry as well as the spectroscopic detection have been performed with the aid of a semiconductor laser [11]. In order to achieve the high frequency selectivities and the narrow linewidths, the photoreactions have to be performed at comparatively low temperatures. Progress, however, on new materials which may also operate at elevated temperatures is on the way.

3. Future Applications: Nonlinear Optical Applications and Electroluminescence Applications

In both the above applications, the polymeric material is not used in a classical sense. In NLO applications the polymer interacts with a light source (typically a laser light source) of high intensity in

order to produce second- and third-order harmonic frequencies [15][16]. Here the high local fields of the electromagnetic waves produce electronic responses of the material – higher order polarizations – which are proportional to E^2 or E^3 (as compared to the normal polarization which is proportional to the electric field E). These higher order materials susceptibilities $\chi^{(n)}$ (with $n > 1$) require special materials and special light stabilities. It is interesting that organic polymers can match inorganic materials in terms of the magnitude of the $\chi^{(2)}$ parameters but their stability has to be further improved.

Fig. 7 gives a comparison of the materials parameters of organic and inorganic materials. From this comparison one can see that the materials parameters of organic solids are, in some instances, equivalent to those of inorganic materials. The only aspect, in which the organic materials need to be improved, is the stability of the materials towards high light intensities and towards orientational relaxations, which destroy the polarity of polymeric $\chi^{(2)}$ materials.

Finally, one of the most novel and maybe most promising fields has been stimulated by the discovery of the photoluminescence effect in organic polymeric materials [17][18]. Here the electroluminescent material is excited electronically (with the aid of an external battery) and emits visible light. Such an electroluminescence application has been pursued many years ago with organic single crystals [19][20]. These early applications, however, were not successful due to the lack of stability of the interfaces between metal electrodes and the organic crystals. The most promising progress has, therefore, been the use of organic polymers, and, especially the use of PPV (polyphenylene vinylene) to improve the stability of the electroluminescent devices and especially the stability of the metal-polymer electrode interfaces. It is probably the dielectric stability of the polymer which led to the progress in the field of this very recent application, and there is some expectation that this recent discovery will have some impact on future display technologies.

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