THE PHOTOCONVERSION OF NAPHTHALENE AND ITS DERIVATIVES IN A POLYMER MATRIX

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UV irradiation of naphthalene in various polymers induces destruction of the macromolecules [1-3] and leads to photoconversion of the sensitizer [1, 4]. The photoconversion of naphthalene in polymethyl methacrylate (PMMA) is a unique "irrepressible" reaction which cannot be hindered by quenching the naphthalene fluorescence as the reaction rate is not determined by the concentration of naphthalene molecules in the excited singlet state found in thermal equilibrium with the medium [4]. Furthermore, the amount of light absorbed by naphthalene determines the rate of destruction of the PMMA ester groups and the quantum yield of this process is close to the quantum yield for the destruction of the sensitizer.

In this work, the photoconversion of naphthalene derivatives, 2,3-dimethylnaphthalene (DMN) and acenaphthene (AN) in PMMA, naphthalene in cellulose triacetate (CTA), polyvinyl chloride (PVC) and in a copolymer of methyl methacrylate (MMA) and naphthyl methacrylate (NMA) containing 3 mol. % NMA unit was examined. The wavelength effect of the activating light, oxygen pressure and solvent, from which the polymer film was prepared, on the quantum yield of the photoconversion of naphthalene in PMMA was examined.

EXPERIMENTAL METHOD

PMMA, CTA and PVC films containing various additives were prepared on a glass surface from solutions in benzene and methylene chloride. The spectrophotometric measurements were carried out on a Specord UV-VIS spectrophotometer, and the luminescence measurements were carried out using a fluorimeter consisting of an SVD-120A high pressure mercury lamp, DMR-2 excitation monochromator, SF-4 recording monochromator, and FEU-38 photomultiplier sensitive in the range from 300 to 800 nm as the light detector. Correction of the luminescence spectrum for dispersion of the monochromator and spectral sensitivity of the apparatus was not carried out. The irradiation was carried out with a DRSh-250 high-pressure mercury lamp with a heat filter filled with distilled water and with BS-4 or BS-5 light filters which transmit light with \( \lambda > 290 \) and \( \lambda \leq 313 \) nm, respectively and with a BUV-30P low-pressure mercury lamp with \( \lambda = 253.7 \) nm. The absolute intensity of the incident light was measured with a ferrioxalate actinometer and monitored by a photovoltaic cell. The study of the kinetics of the process to high degrees of conversion was carried out on samples absorbing \( \leq 10\% \) of the photochemically active light, which permitted us to consider the light intensity within the sample to be uniform.

DISCUSSION OF RESULTS

In Fig. 1, examples of changes during irradiation in the absorption and fluorescence spectra of PMMA films with DMN and AN additives are shown. In Fig. 2, the analogous curves are shown for samples containing naphthalene upon irradiation in the air and in a helium atmosphere. The spectral changes are complex as reaction products are formed which absorb light in the same spectral region as the sensitizer. However, as the optical density of the samples is low, screening of the activating light by the reaction products may be neglected. The instantaneous concentration of sensitizer was determined assuming that the absorption spectrum of the products in the spectral region examined is a monotonic unstructured band which may be approximated by a linear relationship. The technique of determining the concentration was described in detail in earlier work [4, 5]. Irradiation of the samples with partially photodecomposed sensitizer using light with \( \lambda \geq 365 \, \text{nm} \) which is absorbed only by the products does not lead to further consumption of the sensitizer.

In Fig. 3, the kinetic curves are given for the photoconversion of acenaphthene and 2,3-dimethylnaphthalene in PMMA as well as their semilogarithmic transforms which are straight lines. This indicates that the quantum yield for the photoconversion \( \phi \) determined from the slope of the transform does not change during the course of the entire process, that is, the probability of a particle entering the reaction remains constant. The intensity of the sensitizer fluorescence decreases significantly more rapidly than its concentration, which may be related with fluorescence quenching by the reaction products. The drop in the fluorescence quantum yield with unchanging \( \phi \) indicates that the sensitizer is destroyed in the process and that the rate of the process is not determined by the concentration of the species responsible for the fluorescence. This phenomenon is analogous to a phenomenon which we have observed earlier for naphthalene [4].

In order to provide independent evidence to support this hypothesis, we studied the change in the sensitizer concentration during its photoconversion in the presence of the quencher tinuvin P, \( (2(2'-\text{hydroxy}-5'\text{-methylphenyl})\text{benzotriazole}) \) (Fig. 4). Tinuvin P quenches the fluorescence of naphthalene, DMN, and AM. The corresponding energy transfer radii according to Förster [6] are 37, 43, and 45 Å, which agree well with the