The ageing of 1,1-diphenylethene dimer dianions

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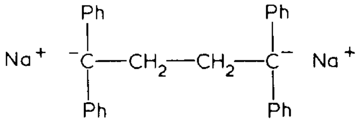
(*Received* 24 *November* 1981)

Solutions of the dimer dianion of 1,1-diphenylethene in tetrahydrofuran have been found to decay but not to transform on storage or on exposure to u.v. light.

Keywords Ageing; transformation; decay; 1,1-diphenylethene; living anions

In an earlier series of papers[1,2] we reported the results of our investigations into the ageing of solutions of living α-methylstyrene oligomers in tetrahydrofuran (THF), and demonstrated that two ageing processes occur simultaneously. These are 'transformation', in which the absorption peak of the living end at 340 nm is slowly replaced by an absorption at longer wavelengths, and 'decay', in which the 340 nm peak slowly disappears but is not replaced. U.v. illumination is essential for the transformation but decay can proceed in the dark.

We now report an investigation into the ageing of solutions of 1,1-diphenylethene dimer dianions in THF. 1,1-Diphenylethene (DPE) reacts with alkali metals in THF to form dimeric dianions[3].



$$Na^{+}\ {}^{-}\underset{Ph}{\overset{Ph}{C}}-CH_2-CH_2-\underset{Ph}{\overset{Ph}{C}}{}^{-}\ Na^{+}$$

In both formation and structure these are analogous to the α-methylstyrene dimer dianion, but because of steric hindrance they cannot homopolymerize.

Experimental

Details of our experimental procedures have been described elsewhere[2]. A solution of DPE in THF was purified by the method of initiation cleansing using a sodium mirror. During this process the blue colour of the benzophenone ketyl impurity was seen, but it did not reappear in the final initiation step. The solution was then divided between two vessels which each incorporated an optical cell. These were stored at 30°C, one in a u.v. lamp and the other in darkness. Changes in the solutions were monitored by periodic u.v.-visible spectrophotometry.

Results and Discussion

Both solutions aged in a similar manner, in that the principle absorption peak at 470 nm fell in intensity and was not replaced by any other peak. Spectra obtained after various storage times are shown in *Figure 1*, where it can be seen that the peak moves slightly to shorter wavelengths at higher ages. Decline of this peak fitted first order kinetics with a rate constant of $2.4 \times 10^{-7}\ s^{-1}$.

The extinction coefficient for the anions was determined by injecting THF containing a known amount of water. The average result of three such injections led to a value for the principle peak at 470 nm of $2.7(5) \times 10^3\ m^2\ mol^{-1}$. This is in close agreement with a report by Szwarc *et al.*[4] A secondary peak at 325 nm had an extinction coefficient of $0.6(4) \times 10^3\ m^2\ mol^{-1}$ which also decayed upon ageing. These are shown in *Figure 2*. With this information, it was possible to calculate that the original anion concentration shown in *Figure 1* was about $6 \times 10^{-3}\ mol\ dm^{-3}$.

Bearing in mind our findings on the role of excess

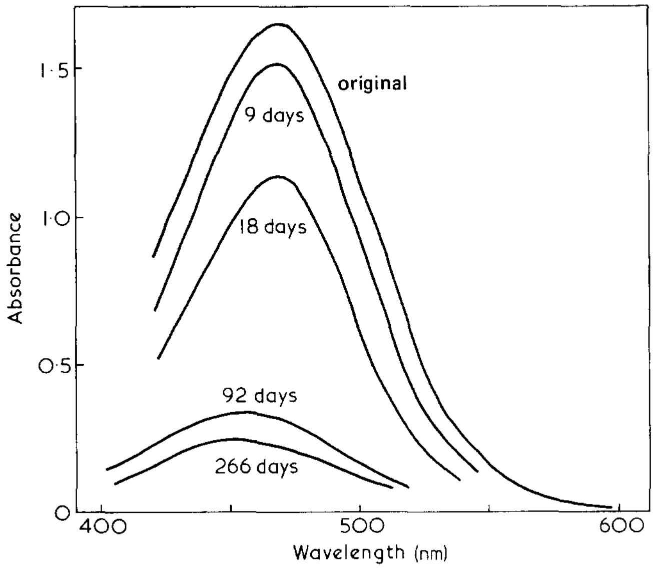


Figure 1 Absorption spectra of disodium dimer of diphenylethene in THF, after ageing for various periods of time. (Path length = 0.1 mm)

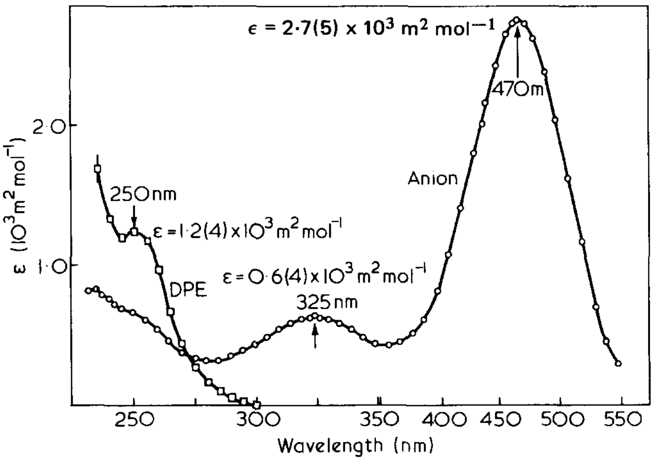


Figure 2 Extinction coefficient spectra for diphenylethene, and for its anions (sodium salt) in THF

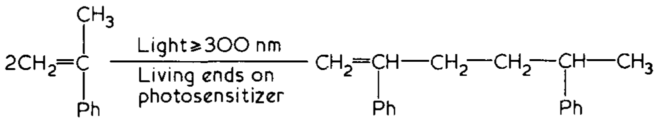
0032-3861/82/040487-02$03.00

monomer in the ageing of α-methylstyryl anions, we determined the extinction coefficient for DPE monomer. After allowing for overlapping absorbances at 250 nm, (*Figure 2*), it can be shown that a small but significant excess of monomer, 2×10^{-3} mol dm^{-3}, was present during ageing.

Only about 60% of the anions were killed by the addition of water, and the remaining anions subsequently decayed at a lower rate than observed with a fresh solution; the first order rate constant was now 1×10^{-8} s^{-1}. A similar decay rate was observed when sodium tetraphenylborate was added to the dianion solution. The ion-pairs in DPE dimer dianion are probably partially dissociated to free ions in THF, in a similar manner to those of α-methylstyrene living ends[5]. If the free anion is more reactive than the ion-pair in the decay reaction, then suppression of ionic dissociation by sodium ions derived from either sodium hydroxide (produced by termination with water) or sodium tetraphenylborate would lead to a lowering of the decay rate.

Implications for α-methylstyrene living ends

We have shown[1,2] that the transformation of α-methylstyrene living ends is dependent upon the photochemical dimerization of monomer to produce 2,5-diphenylhex-l-ene



$$2CH_2{=}\underset{Ph}{\overset{CH_3}{C}} \xrightarrow[\text{Living ends on photosensitizer}]{\text{Light} \geq 300\text{ nm}} CH_2{=}\underset{Ph}{CH}{-}CH_2{-}CH_2{-}\underset{Ph}{CH}{-}CH_3$$

which subsequently is converted by donation of a proton to a living end to another anion which has an absorption peak at 430 nm.

In the case of DPE, the first of these reactions, involving as it does substitution on to the α-methyl group, will clearly not occur. These observations hence support the reaction scheme which we have proposed for the ageing of α-methylstyrene living ends.

The decay process, which occurs both with the DPE and α-methylstyrene dianions, is usually assumed to involve reaction with solvent[6], and hence would be pseudo-first order. The rate of decay is higher with α-methylstyrene dianions (first order rate constant $= 9 \times 10^{-7}$ s^{-1}). However, we have shown[2] that another type of decay involving cyclization could occur in that case. This cyclization requires the addition of another molecule of monomer which is not possible in the case of DPE.

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Studies on syntheses and permeabilities of special polymer membranes: 41. Finger-like cavities in cellulose nitrate membranes from binary organic solvents

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(*Received* 7 *July* 1981; *revised* 16 *November* 1981)

The formation of finger-like cavities in asymmetric cellulose nitrate membranes was investigated by changing the composition of binary mixed casting solvent and the evaporation period during the membrane formation process. The nature of the casting mixture, during the solvent evaporation process, was of coacervated droplets with absorbed water molecules from the atmosphere. Changes in the concentration of cellulose nitrate and the dissolution state of the cellulose nitrate molecules in the evaporation loss of the casting solvent, were clearly related to the formation of the finger-like cavity in the back sponge layer in asymmetric cellulose nitrate membranes.

Keywords Polymer membrane; cellulose nitrate; asymmetric membrane; binary solvent; water absorption; finger-like cavity; membrane formation process

Introduction

Many workers have found that a finger-like cavity was formed in the back sponge layer of various asymmetric polymer membranes[1-8]. We discussed the mechanism[9] and the conditions[10] of the formation of finger-like cavities in cellulose nitrate membranes from various single pure solvents. In general, many polymer membranes for reverse osmosis and ultrafiltration are prepared from 2 or more mixed casting solvents in order to improve the membrane performance. This method, which uses the mixed casting solvent, can finely control the conformation of the polymer molecules in the casting mixture during the solvent evaporation process. Consequently, it is possible to control the factors that have effect on the permeation characteristics, i.e., pore size pore number in the dense surface layer and thickness of the dense surface layer. For the purpose of investigating the structure of cellulose nitrate membranes from a mixed solvent, in particular this communication deals with the formation of a finger-like cavity in the back sponge layer.

0032-3861/82/040488-04$03.00