PHOTOTRANSFORMATION OF THE GLYCIDYL ETHER OF SALOL BY IR SPECTROSCOPY

A. M. Noskov and N. I. Novikov

Phenyl salicylate (salol) or other aromatic salicylates are effective photostabilizers of polymers [1]. It has been shown [2] that salol present in a polymer matrix under the action of UV irradiation undergoes a Fries photorearrangement, the main products of which are dihydroxybenzophenones

Thus the stabilizing action of aromatic salicylates is secured by their photoconversion products in the polymer—hydroxy benzophenones, the mechanism of the protective action of which has been well studied [3]. Both products of reaction (1) are excellent photostabilizers of polymers [3]. Since the described phototransformation operates throughout the entire duration of irradiation, the presence of phenyl salicylate gives rise to self-stabilization of the polymer. Despite the small amount of additive, 0.1-4.0%, self-stabilization constitutes a marked competition to the degradation process [1, 2, 4].

The self-stabilization effect will be greater where in the polymer chain between the aromatic rings an ester group is present. During UV irradiation of aromatic polyesters a Fries rearrangement is possible with formation of o-polyhydroxybenzophenone structures. Similar self-stabilization has been detected in a series of polyesters [5-9]. The discussion given in review articles [10, 11] of this method of photostabilization showed that despite the low quantum yield of formation, stabilizers which form part of the chain of a high-molecular linear polymer have preference over extrinsic low molecular weight photostabilizers since the latter in operation can be decomposed, volatilized, or leached out by liquids. It may be expected that the occurrence of a Fries rearrangement in a network polymer will promote a greater effectiveness of self-stabilization than in a linear polymer.

In the present work the results are discussed of an IR spectroscopic study of the possibility of the occurrence of a Fries rearrangement in a cross-linking epoxide oligomer (EO). The material studied was the glycidyl ether of salol (GES)

GES was synthesized by the method given in [12] by condensation of salol with epichlorohydrin in an alkaline medium at 70°C. n-Hexane was used as solvent. The GES obtained had boiling point 185-205°C (655 Pa), epoxide group (EG) content 16%, $d_4^{20}$ 1.2010, $n_4^D$ 1.5253, $M_D^{theor}$ 69.629, $M_D^{found}$ 68.950. As a model compound we used the glycidyl ether obtained by the above indicated method by condensation of tetrahydroxybenzophenone with epichlorohydrin in an alkaline medium at 70°C. Acetone was used as solvent. The product had the following characteristics: $d_4^{20}$ 1.1071, $n_4^D$ 1.5314, $M_D^{theor}$ 101.388, $M_D^{found}$ 100.936. The presence of an EG and hydroxyls was confirmed by IR spectroscopy. This indicated that the synthesized compound was the glycidyl ether of trihydroxybenzophenone (GETB) and therefore contained the o-hydroxybenzophenone structure in the molecule together with the glycidyl group.

The UV irradiation of the GES was carried out in a specially constructed irradiator, a diagram of which is given in Fig. 1. The liquid ether was placed in a round-bottomed quartz flask of 50 ml volume which was situated 10 cm from a PRK-4 quartz-mercury lamp. A system of cylindrical mirrors was used to enhance the irradiance of the sample. With the aim of preventing heating of the sample during irradiation, the flask was...
cooled by means of a fan. In order to record transient changes the IR spectrum of the GES was measured periodically. Recording of the spectra was also carried out directly during irradiation. For this purpose a chamber was used which was attached to the IR spectrophotometer, the design of which has been described in an earlier paper [13]. Compared to the earlier design certain changes were made: a microcell for irradiation of the liquid samples with an absorption layer thickness of 20 μm was constructed, and in the chamber a square-shaped reflector was fitted which enhanced the total irradiance of the sample. Choice of material for the windows of the cell was particularly difficult: one of the windows should be transparent to IR and UV radiation. Recording the electronic spectra showed that a NaCl plate of 3 mm thickness, the optical density of which in the wavelength region of 0.20-0.80 μm did not exceed 0.17, could be used for this purpose. Study of the thermal Fries rearrangement was carried out in the same chamber with a vertical arrangement of the cell with the sample.

IR spectra of the GES were obtained at temperatures of 60-200°C with 20°C intervals, and for each temperature until fixation of the spectrum the sample was maintained for 1 h. In all cases no changes of the spectrum occurred which indicated that thermal Fries rearrangement of GES is not possible. In subsequent experiments the sample was disposed at an angle of 45° to the propagation direction of the IR beam and the surface facing the quartz window was subjected to UV irradiation for 10 h continuously, the spectra being recorded every 15 min. Changes in the IR spectra began after the first few minutes of irradiation (Fig. 2). They are expressed in the emergence of a band due to OH-groups, with a center of density at 3400 cm⁻¹, the appearance of a band at ν = 943 cm⁻¹, and a decrease in optical density of the band due to stretching vibrations of the EGs at ν = 917 cm⁻¹. The absence of thermal rearrangement of GES does not exclude the possibility of a thermal activation of the photorearrangement. It is known that photochemical reactions in polymers are often accelerated under thermal action. For example the rate of oxidative degradation of the cured diglycidyl ether of diphenylolpropane increases with slight increase in temperature [13]. Therefore the IR spectra of GES were recorded after continuous UV irradiation for 8 h at temperatures of 60 and 80°C. The changes in the spectra were no greater than those obtained previously at room temperature, which demonstrates the absence of a thermal activation of the Fries photorearrangement of GES. Therefore subsequently only the photoconversion of GES was studied.

From the curves of Fig. 2 it is seen that the 3400 cm⁻¹ band indicating photorearrangement appears close to the two bands due to hydroxyl absorption with maxima at 3210 and 3470 cm⁻¹. The first band can be assigned to the vibrations of intermolecularly bound OH-group structures containing a secondary alcohol group. These latter are formed as a by-product during the synthesis of GES

\[
\text{I} \xrightarrow{T} \text{II}
\]

The second band is apparently due to the inclusion of the OH group of structure II in an intramolecular hydrogen bond