INTERACTION OF LIGNOSULFONATE WITH A SYNTHETIC POLYMER

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The interaction of a lignosulfonate with the product of the alkaline hydrolysis of nitron fiber has been studied by gel chromatography. It has been shown that in the interaction product the reactants are present in a ratio of 100:1 (hydrolyzed nitron lignosulfonate).

In the literature a wide range of reactions between two polymers, mainly synthetic ones, forming polyelectrolyte complexes has been described [1]. Publications are known that consider the interaction of a lignosulfonate with cation-active polymers, as the result of which both insoluble and readily water-soluble products are formed. In particular, the formation of polyelectrolyte complexes on the interaction of lignosulfonates and poly(N,N-dimethylaminoethyl methacrylate) has been studied [2, 3].

The processes involved in the formation of polyelectrolyte complexes of lignosulfonates with a polybase are of interest in connection with the practical use of mixtures of lignosulfonates with nitrogen-containing polyelectrolytes in the national economy [4, 5]. In the present paper, we consider the interaction of a lignosulfonate (LS) with a product of the alkaline hydrolysis of nitron [polyacrylonitrile fiber] (HN).

As shown by IR spectroscopy and elementary analysis, hydrolyzed nitron consists of a product of the incomplete hydrolysis of the acrylonitrile units of the polymer. Nitrogen-containing functional groups are therefore present in the HN macromolecules, and they are polyelectrolytes [6].

Since the interaction of a lignosulfonate with hydrolyzed nitron should lead to an increase in molecular mass, we used gel chromatography to investigate this system. Figure 1 gives chromatograms of reaction mixtures obtained at various times of heating and without heating. Where the initial reactants were mixed at room temperature a single peak coinciding with the peak of the initial LS was present on the gel chromatogram. On heating to 90°C, a second peak appeared in the region of high molecular masses, and with an increase in the time of heating the HN—LS reaction mixture the proportion of the second peak increased.

It may be mentioned that the second peak is narrower than the first. It has been shown [2] that on the interaction of a lignosulfonate with the synthetic polymeric base poly(N,N-dimethylaminoethyl methacrylate) the molecular mass of the LS has a pronounced effect. It may be assumed from the results shown in Fig. 1 that LS macromolecules of a definite molecular mass bind preferentially with hydrolyzed nitron.

Figure 1 also shows the results of the gel chromatography of mixtures of HN with lignosulfonate obtained one day and 1.5 months after mixing. The second peak can be seen after one day, and its proportion increases with time.

Chromatograms of the HN—LS system taken after five-hour heating and after one month were also obtained. The two were identical. Consequently, the interaction of hydrolyzed nitron with lignosulfonate is probably complete after five-hour heating at 90°C.

Thus, the reaction between hydrolyzed nitron and lignosulfonate requires the reaction mixture to be heated or to be kept for a certain time at room temperature. This is obviously due to the highly viscous state of the reaction mixture under the concentration conditions investigated.

In the experiments described above, the initial reactants were used in a ratio of 1:1 (in grams). On all the chromatograms obtained (Fig. 1), in addition to the peak of the reac-

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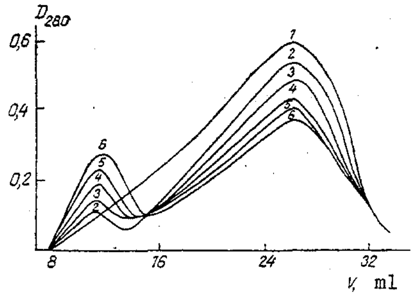

Fig. 1. Gel chromatograms of the HN–LS system at different reaction times; HN:LS ratio = 1:1 (in grams): t = 90°C: 1) LS; 2) LS-HN, τ = 0.5 h; 3) HN-LS, τ = 1 h; 4) HN-LS, τ = 2 h; 5) HN-LS, τ = 3 h; 6) HN-LS, τ = 5 h; 1 month; t = 20°C: 1) LS-HN, τ = 0; 2) LS-HN, τ = 1 day; 5) LS–HN, τ = 1.5 months.

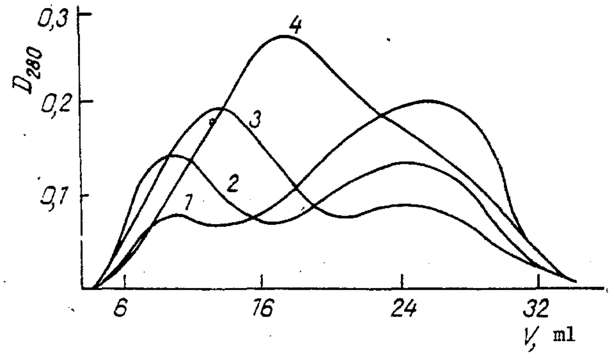

Fig. 2. Gel chromatograms of the HN–LS system as a function of the ratio of the reactants NH:LS (in grams) (τ = 4 h, t = 90°C). 1) 10:1; 2) 20:1; 3) 40:1; 4) 100:1.

tion product, a large peak coinciding with the peak of free LS that had not reacted was observed. In order to determine the ratio of HN and LS in the reaction product we subjected to gel chromatography reaction mixtures with various ratios of the components – HN:LS = 10:1, 20:1, 40:1, and 100:1.

Figure 2 shows the chromatograms obtained. It can be seen that with an increase in the HN:LS ratio the relative size of the peak of the interaction product increased and that of the free lignosulfonate decreased correspondingly. At the same time, a small shift of both peaks in the direction of smaller molecular masses can be seen. It is likely that the lignosulfonate macromolecules with a higher molecular mass take part in the interaction with the hydrolyzed nitron first. In this case, when there is a large excess of the LS component only the high-molecular-mass part of the lignosulfonate used reacts. With a decrease in the excess of lignosulfonate the whole of the high- and part of the low-molecular-mass fraction enter into the reaction. When a HN:LS ratio of 100:1 is reached a single peak is observed on the gel chromatogram. Consequently, in the last case all the lignosulfonate macromolecules pass into the composition of the reaction product. All this leads to a shift of the peaks and to a decrease in the molecular mass of the product with an increase in the HN:LS ratio.

It can be seen from Fig. 2 that the peak of the product of the reaction of hydrolyzed nitron with lignosulfonate is located in the region of higher molecular masses than the peak of the free lignosulfonate. The width of the product peak indicates a fairly wide molecular mass distribution.

Thus, the results obtained permit the assumption that it is the high-molecular-mass part of the lignosulfonate that first enters into interaction with hydrolyzed nitron. In the reaction product the reactants are present in a ratio HN:LS = 100:1 (in grams).

EXPERIMENTAL

Alkaline Hydrolysis of Nitron Fiber. A mixture of 10 g of nitron fiber and 90 ml of 5.5% NaOH solution was heated at 102°C for 5 h. Then 0.1-1 g of lignosulfonate was added, and heating at 90°C was continued for 0.5-5 h. Powdered lignosulfonate from the Solikamsk TsBK [Pulp and Paper Combine] was used.

Samples for gel chromatography were taken directly from the reaction solutions. Gel chromatography was conducted on a column (1.1 × 40 cm) filled with Sephadex G-200. The solvent used was 0.5 M NaCl solution.

Optical densities were recorded on an SF-26 spectrophotometer at the wavelength λ_{max} = 280 nm.

LITERATURE CITED

1. A. B. Zesin and V. B. Rogachev, Advances in the Chemistry and Physics of Polymers [in Russian], Moscow (1973), p. 3.
2. G. M. Shul'ga, R. I. Kalyuzhnaya, L. N. Mozheiko, F. V. Rekner, A. B. Zezin, and V. A. Kabanov, Vysokomol. Soedin., 24, Ser. A, No. 7, 1516 (1982).
3. O. M. Shul'ga, A. B. Zezin, R. I. Kalyuzhnaya, L. N. Mozheiko, and F. V. Rekner, Khim. Drev., No. 2, 63 (1981).
4. G. M. Shul'ga, L. N. Mozheiko, F. V. Rekner, and A. Ya. Metra, Izv. Akad. Nauk Latv. SSR, No. 5, 126 (1980).
5. V. N. Sergeeva, G. M. Tarnarutskii, N. V. Gribanova, and G. M. Telysheva, Khim. Drev., No. 3, 3 (1979).
6. K. S. Akhmedov, S. A. Zainutdinov, I. K. Sataev, and U. Rakhimov, Information Report of the Uzbek SSR Academy of Sciences, No. 69 [in Russian], Fan, Tashkent (1972).

INSECT PHEROMONES AND THEIR ANALOGS.

XLVII. SYNTHESIS OF 11-OXODODECA-3,6-DIYNOIC ACID — THE ACYCLIC PRECURSOR OF A MACROLIDE COMPONENT OF PHEROMONES OF Oryzaephilus mercator AND O. surinamensis

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A new approach is proposed to the synthesis of 11-oxododeca-3,6-diynoic acid — the acyclic precursor of a macrolide component of pheromones of *Oryzaephilus mercator* and *O. surinamensis* — from the readily available tetrahydropyran or allylacetone via the intermediate 5-bromo-2,2-ethylenedioxypentane.

The synthesis of one of the macrolide components of the aggregation pheromones of the grain beetles *Oryzaephilus mercator* and *O. surinamensis* — dodeca-3Z,6Z-dien-11-olide (I) — requires 11-oxododeca-3,6-diynoic acid (II). It has been obtained previously from derivatives of but-3-yn-1-ol and hept-6-yn-2-ol [1, 2]. We have developed a new approach to the synthesis of the oxoacid (II) from tetrahydropyran (III) or allylacetone (IV), both readily available, the transformation of each of which leads to one and the same key synthon — 5-bromo-2,2-ethylenedioxypentane (V). (see scheme on next page).

The opening of the ring of (III) under the action of HBr and H_2SO_4 formed 1,5-dibromopentane (VI), which was selectively dehydrobrominated by heating in hexametapol, forming 1-bromopent-4-ene (VII) with moderate yield. The oxidation of the latter with molecular oxygen in the presence of $PdCl_2$—CuCl in aqueous THF gave 5-bromopentan-2-one (VIII), which was converted into its acetal (V).

The alternative pathway for the synthesis of compound (V), from the ketone (IV), includes the stage of ozonolysis of its ethylenedioxy derivatives (IX). The 2,2-ethylenedioxypentan-5-ol (X) so formed was smoothly converted into the desired bromide (V), the yield of which calculated on the initial (IV) was 63.4%. Since the overall yield (26.6%) of synthon (V)

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