

PLASMA POLYMERIZATION OF STYRENE AND BENZENE IN GLOW DISCHARGE*

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Thin films of styrene and benzene were prepared by plasma polymerization in a glow discharge under static conditions. The films formed in various places of the discharge differed in their growth rate. The IR spectra showed an amorphous polymer and ESR the presence of a high number of free radicals gradually decaying upon contact of the film with air.

ПЛАЗМЕННАЯ ПОЛИМЕРИЗАЦИЯ СТИРОЛА И БЕНЗОЛА В ТЛЕЮЩЕМ РАЗРЯДЕ

С помощью плазменной полимеризации приготовлены в статическом тлеющем разряде тонкие плёнки стирола и бензола. В различных местах разряда эти плёнки имеют различную скорость образования. Инфракрасные спектры показали присутствие аморфного полимера, и электронный спиновый резонанс показывает наличие большого числа свободных радикалов, медленно исчезающих при соприкосновении плёнки с воздухом.

1. INTRODUCTION

Recently thin polymer films are being prepared in plasma mostly in an R. F. glow discharge [1]. The films produced in such a way have several advantages, first of all a high thermal stability, chemical resistance to acids, bases, and organic solvents, very good adhesion properties, and they are practically free from pores [2—4]. These properties predetermine the polymer films obtained in plasma for wider applications in practice, namely for thin insulating or protective coatings, for obtaining thin films of a semiconductive nature, or preparing reverse osmotic membranes [5].

Some attempts at preparing polymer films also in a D. C. glow discharge were made [6,7] but there was not paid due attention to this procedure because of the problems connected with production in larger amounts. Parts of the D. C. glow discharge, however, are attractive from the viewpoint of polymer films production,

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such as the positive column and mainly the part near the cathode. It was this reason that we paid in this paper attention to the formation of polymer films in various parts of the D. C. glow discharge. The films were prepared from monomers of styrene and benzene in a closed system. Preparation under such conditions is interesting also for the fact that a pressure change in the system can provide certain information on the mechanism of the formation of the films [8]. The obtained films were investigated by ESR and IR spectroscopy.

II. EXPERIMENTAL METHODS

The polymer films were obtained in an apparatus schematically drawn in Fig. 1. The actual working volume was a recipient of 17 l. the electrodes were round copper plates with a surface of 38 cm², the gap could be changed arbitrarily. The D. C. glow discharge was excited by a stabilized voltage source and the discharge varied by means of a rheostat *R*. Before working the apparatus was evacuated to a pressure of about 10⁻³ Pa with a diffusion pump DV, then the monomer from the reservoir *M*, or from the other one Ar was fed as carried gas up to the corresponding pressure measured by an oil-filled U-tube pressure gauge. With the aid of the U-tube pressure gauge the total pressure change in the closed system could be observed, too.

The amount of free radicals in polymer films obtained in the glow discharge was determined by an ESR spectrometer developed by Š. Šurka at the Department of Experimental Physics of Faculty of Natural Sciences, Comenius University, Bratislava.

The IR spectra of polymer films were scanned on Carl Zeiss UR-10 and Perkin Elmer PE-180 spectrometers. The spectra were obtained from films applied on slides by the reflection technique on the one hand, and from the material scraped from the slide or from the electrode by the KBr tableting technique on the other hand. The obtained spectra were compared with those of polymers prepared by the conventional method.

III. RESULTS

The polymerization by means of the D. C. glow discharge in monomer vapours proceeded in the presence of argon as carrier gas. From the results it follows that the amount of Ar has no effect on the structure of the polymer films formed on the electrodes and also on the slides successively placed in the cathode region, the positive column and the anode region of the glow discharge. Within the same time the greatest amount of polymer formed on the cathode and the smallest on the

anode, while the analysis of IR spectra showed no difference in the quality of these samples.

All the polymer films of styrene and benzene were obtained with a 35 mm electrode gap. The discharge was ignited at the voltage $U_d = 600$ V and during formation of films a constant discharge current $I_d = 10$ mA current density $j = 0.25$ mA cm⁻² was maintained, namely by increasing voltage on the electrodes.

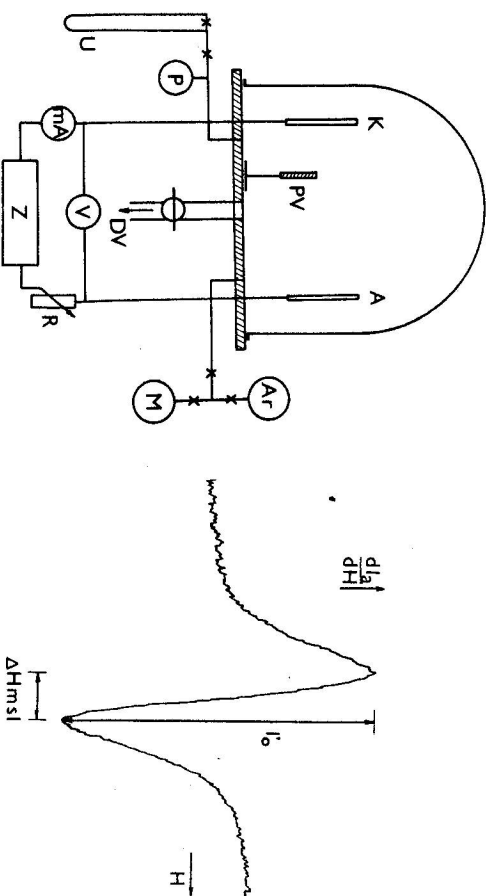


Fig. 1. Apparatus for obtaining polymer films in D. C. glow discharge. A and K electrodes, PV polymer film, Z stabilized voltage source, M and Ar reservoir of monomer and argon, resp., DV diffusion pump, P Penning vacuum gauge, U oil-filled U-tube pressure gauge.

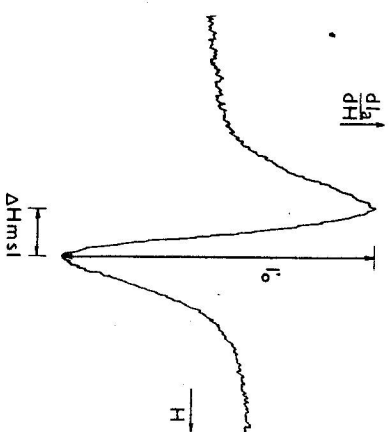


Fig. 2. Typical ESR signal in thin film of polystyrene formed in glow discharge.

The amount of free radicals was determined by ESR for the samples from the cathode obtained in pure styrene, in a mixture of Ar and styrene, and in a mixture of air and styrene. All the samples were in contact with air for 15 min (time necessary for handling the sample). A typical ESR signal of polystyrene film is in Fig. 2. The given samples of polystyrene, however, did not markedly differ in the amount of radicals, the level of which was 5×10^{16} r./g. In contact with air during three days the amount of free radicals rapidly diminished. In polymer films obtained only in benzene vapours the number of free radicals was very high, 7×10^{18} r./g., and in the sample obtained in a mixture of air and benzene considerably lower 5×10^{16} . In contact with air the amount decreases already after one day below 10^{15} r./g.

The IR spectrum of polystyrene prepared in the discharge is in Fig. 3, in

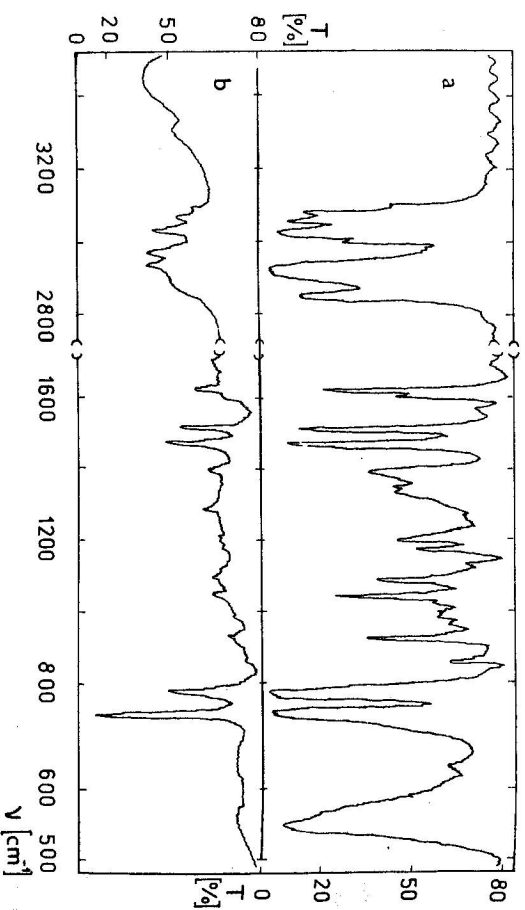


Fig. 3. IR spectra of polystyrene: a) atactic, b) polymerized in plasma of glow discharge.

comparison with that of polystyrene obtained by the conventional method. The spectra are in the range from 500 to 3500 cm^{-1} and the calibrated wave numbers used are from [9, 10]. By comparison it follows that the polymer has a chain containing above 100 monomer units, which is proved by the appearance of absorption bands between 900 and 1100 cm^{-1} not present in the monomer spectrum. The absorption bands at 700 cm^{-1} , corresponding to a monosubstituted aromatic ring, have a similar behaviour. Compared with the spectrum of conventional polystyrene there are in this spectrum of conventional polystyrene there are

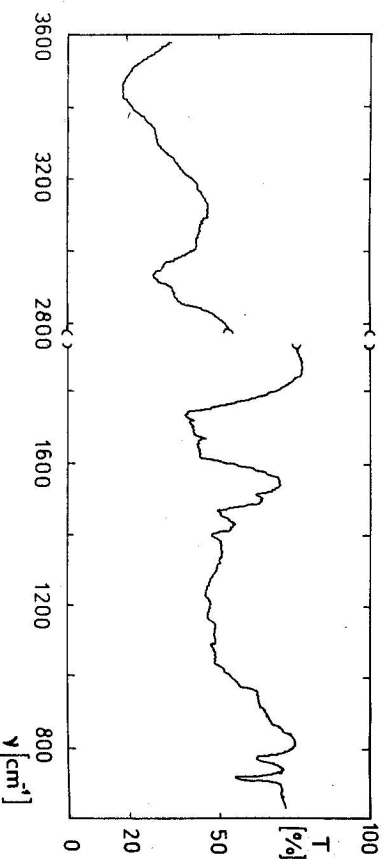


Fig. 4. IR spectrum of benzene polymerized in plasma of glow discharge.

in this spectrum three absorption bands corresponding to an amine group —NH at 3300 cm^{-1} , an —OH group at 3450 cm^{-1} and a carbonyl group C=O at 1700 cm^{-1} . It is characteristic of the IR spectrum of polymer obtained from benzene (Fig. 4) that the benzene spectrum disappeared. The bond vibrations of the aromatic ring in the region 3030 to 3060 cm^{-1} are very weak and those of the —CH_2 group markedly increase in the region 2850—2925 cm^{-1} . In principle the polymer maintains the aromatic structure, which is monosubstituted, as proved by bands at 700 and 760 cm^{-1} . The obtained substance is polymerized only partly according to the presence of an —OH group at 3450 cm^{-1} and the wide range of etheral bonds 1050 to 1270 cm^{-1}). The sample is considerably degraded.

IV. DISCUSSION

In a D. C. glow discharge styrene gives polymers maintaining the fundamental skeleton vibrations a monosubstituted aromatic ring with an attached aliphatic chain. The formation of the polymerized substance from benzene is conditioned by the partial cleavage of the aromatic ring. The D. C. glow discharge, mainly in its part near the cathode, owing to the presence of energetic particles can cause fission of monomer molecules into fragments with their subsequent incorporation into the film. Apart from this the observed oxidative-degradation mechanism of the reaction also makes it difficult to envisage in greater detail the mechanism of formation of such polymer films. Even though the conditions in the part near the cathode are rather complicated since in the formation of the polymer film there appear electrons, UV radiation, positive ions, excited atoms and molecules, free radicals and their recombination on the surface of the film, we can draw the conclusion that in the glow discharge polymerization free radicals play a significant role as proved by their high number in the obtained polymer films, too.

The relatively good solubility of films, formed at current densities below 0.5 mA cm^{-2} and within a short period, indicates that the polymer is linear or slightly crosslinked. In contact with air the solubility and the number of free radicals decrease, which proves that the radicals react with air particles and increase the degree of crosslinking. The films prepared at current densities above 1 mA cm^{-2} have a similarly higher degree of crosslinking.

The IR spectra of the styrene sample prepared in plasma show a nearly consistent polystyrene structure with an indication of fragmentation due to discharge. The presence of OH , CO and NH groups is the consequence of the reaction of free radicals with O_2 and N_2 in air, and of the incorporation of the products of these reactions into the film. The obtained polystyrene film is amorphous, without crystalline structure, as it follows from the absence of an absorption band at 983 cm^{-1} .

The IR spectrum of the polymer obtained from benzene has weak absorption

bands of the aromatic ring and a marked absorption band of the CH_2 group, and so during its formation in the discharge the aromatic ring had to be degraded to fragments with their subsequent incorporation into the structure of the film.

The high number of free radicals, in principle equal in all polystyrene samples, indicates that the free radicals are the particles playing a decisive role in the mechanism of formation of these films. The free radicals, present in the film, decay in contact with air as a consequence of the combination with atmospheric oxygen and nitrogen.

The number of free radicals, substantially higher in the polymer film obtained from benzene vapours, can be explained by fission of the benzene rings due to the glow discharge. On the other hand this is not the case in the formation of polystyrene, thus there is a higher possibility of formation of a greater number of free radicals in comparison to styrene, where they can be formed only on the aliphatic chain. Equally as in the case of polystyrene, the radicals are partially bonded in contact with air and so the total degradation of the structure of the polymer film obtained from benzene increases.

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