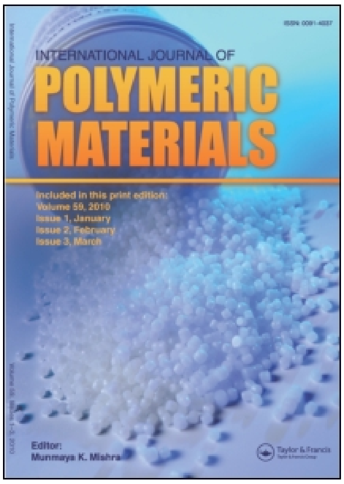

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DIFFUSE REFLECTION SPECTROPHOTOMETRY (DRS) FOR RECOGNITION OF PRODUCTS OF RADIOLYSIS IN POLYMERS

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The mechanism of radiolysis of polymers can be recognized by product analysis and identification of reaction intermediates, followed by their determination. Among product analysis methods, the most appropriate is spectrophotometry. Due to the poor transparency of polymers occurring mostly as powders from the polymerization line, and the opacity or poor transparency of most processed polymers, the best mode of measurement is diffuse reflected light spectrophotometry (DRS) in UV-VIS. Application of the DRS method to simple systems of low molecular weight and the comparison with the transparent system of the same chemical composition has shown a full veracity of the approach and the application to polymer systems is justified. The important feature of the DRS method is the measurement of absorption spectra against unirradiated polymer sample. Therefore only products of radiolysis are shown, because optical disturbance at the surface texture of the sample is compensated and does not interfere with the recorded spectrum. Optical spectra of irradiated polymers are compared with EPR spectra, leading to a more precise identification of products. Several polymeric systems investigated in our laboratory are listed and one of the systems is presented in the paper in detail: radiation chemistry of virgin polypropylene investigated by the DRS, EPR and gravimetry (chain reaction of oxidation, initiated by us pulse of radiation, but proceeding for several months, in the polymer exposed to air). The diffuse reflected light spectrophotometry is very often a key method among other methods of investigation and has proved its usefulness in the investigation of radiation chemistry of many classes of polymers.

Keywords: chain reactions in polymers, diffuse reflection spectrophotometry, DRS, electron paramagnetic resonance, EPR, oxidation of polymers, polypropylene, radiation chemistry of polymers, spurs in polymer irradiation

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1. INTRODUCTION

The mechanism of radiolysis of polymers can be recognized by product analysis and identification of reaction intermediates, followed by their determination. Among product analysis methods, the best suited for the quality and quantity of formed compounds and groups is absorption spectrophotometry in UV-VIS. It is adequate to investigations in radiation chemistry, due to usually high ε values (molar extinction coefficients, molar absorptivities) of reaction products induced by radiation. These values are higher by 3–4 orders of magnitude than molar absorptivities in the IR region. The concentration of products in radiation processing at doses, as applied, *e.g.*, in radiation sterilization of polymers, is low [1]. Therefore the UV-VIS spectrophotometric data are extremely useful in basic research and applications.

Sensitivity of detection of radiolytic changes in irradiated polymers depends on the molar extinction coefficient of the products. Species formed by the action of ionizing radiation have usually molar extinction coefficients (ε) in the order of hundreds and thousands of M^{-1} cm^{-1}, thus allowing observation of radiation effects sometimes even after an absorbed dose as low as 10 grays. Unfortunately, the conventional spectrophotometry in UV-VIS transmitted light-spectrophotometry can be successfully applied only to reasonably transparent polymer preparations. Already a small haze appearing with the change of polymer composition (cf., *e.g.* [2]) can render the measurements impossible. Conventional spectrophotometry requires reasonably transparent samples, *e.g.*, of background absorption and/or turbidity not exceeding 2 units of optical density (OD). Some modern spectrophotometers offer a tolerance of OD of background up to 5, but high dissipation of analytical light impairs the chances of spectral investigations. In the case of polymer systems, conventional spectrophotometry would mean a limitation of experimental field almost exclusively to transparent polymeric films. To meet the need for recording the full spectra of irradiated polymers, we have applied diffuse reflectance spectrophotometry (DRS), the method in which light reemitted from inside the sample carries an information of absorbing species. To our knowledge, this approach has not been applied to irradiated polymers yet, as concerns the UV-VIS range, where the poor transparency is common.

No single method, however efficient, can solve basic and applied problems of radiation chemistry of polymers. Other methods applied in studies on the radiation chemistry of polymers in our Laboratory (mainly electron paramagnetic resonance EPR, also called electron spin resonance ESR, gravimetric measurements of chain oxidation of reactive polymers *etc.*) are not sensitive to the opacity of the material.

2. DIFFUSE REFLECTED LIGHT SPECTROPHOTOMETRY IN RADIATION CHEMISTRY

As the DRS method is seldom used in radiation chemistry so far, it needs closer explanation of its principles. Figure 1 shows the principle of the method of diffuse reflectance spectrophotometry. The reflection from metallic surface (left part of the diagram), so called specular reflection, involves a few atomic layers only and explains the color of certain metals, *e.g.*, of gold and copper. The reflected spectrum is also interesting in construction of optical devices, in which as high a yield of reflection is desired as possible, *e.g.*, in selected regions of infra red. In applications to radiation chemistry, the specular reflection is of no use; on the contrary, every effort is made to get rid of it, as it does not carry any information originating from the inside of the sample. The next example (in the middle of the Figure) shows a layer of polymer, illuminated with a beam of light. According to laws of optics, the analyzing beam falling diagonally on the surface of transparent (even slightly translucent) material is partly reflected (specular reflection) and partly refracted into the material. This fraction of light is the most important, because due to internal reflections, it is able to leave the sample, but is at attenuated by absorption by species formed in the sample.

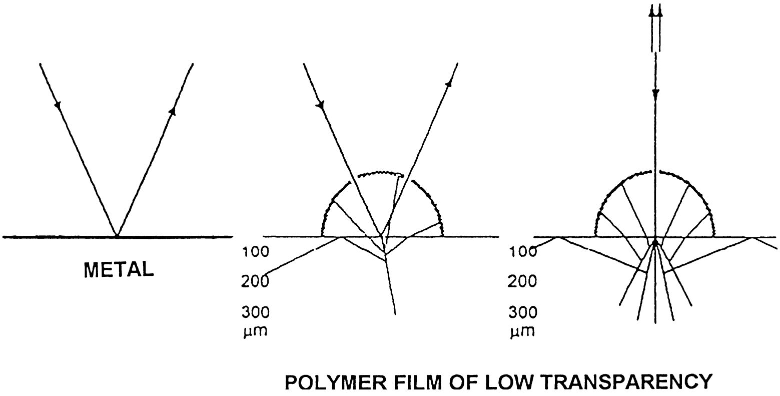

FIGURE 1 Simplified picture of the origin of diffuse reflection spectroscopy. See explanation in the text.

The escaping beam carries the important information about the absorption at particular wavelength. The third scheme depicts the vertical beam of analyzing light. The reflected specular beam escapes along the same route as the incident beam. The beam intruding inside the sample causes similar phenomena as in the case of diagonal beam, *i.e.*, produces reflected stray light, containing information about new compounds and/or destruction of the existing one in the sample.

The equipment for this measurement is available commercially either as attachments to the basic spectrophotometer, or as independent, sometimes even hand-held instruments. Only few instruments are well adapted to the application of that idea, because our specific demand is to compare the irradiated sample and unirradiated one in a single measurement. Such procedure eliminates the unnecessary information about structures and textures of the sample and yields the spectrum of the difference between samples, which is the spectrum of species formed or modified by the energy of the absorbed ionizing radiation.

The diagram shows that the amount of escaping light is small, and the losses are substantial, due *e.g.*, to total internal reflections of a nature similar to light guides (in our system the light-guide-type of transportation is not desired!). Therefore efforts are made to collect as much of re-emitted light as possible, *e.g.*, by placing the detectors in places where the emission is largest, although a certain compromise must be reached, because the distribution of light depends on many factors involved, including not only the properties of material, but also the wavelength. The best collection of light is secured by the inside wall of a hollow sphere. Usually the optimization is based on the reflection of barium sulfate. In the system chosen in our Laboratory the angle at which the analytical light beam is striking the sample at 10 degrees.

In conventional DRS measurements, *i.e.*, not connected to radiation effects, *e.g.*, in order to describe the color of a sample objectively, there is a general trend to make the measurement twice: first to measure the reflection spectrum of the sample, next to record the response to a standard of white, *e.g.*, of barium sulfate and later to calculate, nowadays with the help of computer, the difference between both spectra. This way is satisfactory for most of problems encountered in general chemistry. However, in radiation chemistry that solution seems to be unnecessary complicated, because it involves an additional step which lowers the precision of the measurement. Such two way measurement is: irradiated sample *vs.* barium sulfate, then unirradiated sample *vs.* barium sulfate, followed by comparison of spectra. The spectrum against barium sulfate is difficult to interpret, because it is disturbed by an influence of the structure and texture of the sample. The direct "double beam – double sample" measurement yields immediately the differential spectrum which can be assigned only to the species formed by ionizing radiation energy. All spectra in the present paper are recorded with this superior system.

3. QUANTITATIVE ASPECTS OF THE DRS METHOD

It is a fortunate situation in radiation chemistry, where we can compare an irradiated sample *vs.* unirradiated one, compensating all factors influencing spectrum, like the roughness of the surface. Such simple measurement may be performed only with spectrophotometers of specific construction. We have found that only two spectrophotometers of leading firms fulfill the requirements: These are double beam apparatuses with the light integrating sphere with two windows – the first for the reference, the second for the sample. The beam of analytical light probes alternately the irradiated and unirradiated samples in the sphere, recording only the difference of absorptions at defined wavelengths. The dedicated computer program determines the wavelengths of maxima of bsorption bands, allows to change scales to record results of other easurements for comparison *etc.* The measurement is as simple as in conventional spectrophotometry and consists of placing the unirradiated and irradiated polymers at respective windows in the instrument.

The absorption spectrum of irradiated sample is measured against the unirradiated reference, otherwise identical with the irradiated sample, as concerns the turbidity, texture of the surface, *etc.*

Although the instrumental side requires the modern state of art of optoelectronics and computer assisted acquisition and data processing, the theory of diffuse reflection spectroscopy dates back almost to the first quarter of the XX Century. Kubelka and Munk [3] and later Kubelka [4] has developed the theoretical treatment of the phenomenon of diffuse reflection, leading to equations connecting the new approach with traditional equations of extinction, known as Lambert-Beer law. New equations involve ε, the molar extinction coefficient. However, a simple determination of ε from the diffuse reflection measurement is not possible, because Kubelka-Munk function F(R) involves coefficient S describing scattering coefficient of the matrix. Therefore the calculation of ε is difficult especially in the case of polymers, and in some cases seems to be impossible to solve at the time being. Nevertheless, the comparative value of changes of spectrum after irradiation, effect of reactions with gases, bleaching by light *etc.*, is of a great value. Diffuse reflectance spectroscopy went early into monographs [5,6] but did not find its way into the field polymer chemistry.

Before starting the DRS studies on polymers, we have tried the capabilities of the method on simpler systems, *i.e.*, on the measurement of the radical anion $CH_3C^{\bullet}HCO_2^-$ in different matrices. The radical in polyethylene matrix has been investigated by DRS ($\lambda_{max} = 350\,nm$); it is a basic species for alanine dosimetry [7], and the single crystal of alanine has been investigated by conventional spectrophotometry. In that version the molar extinction coefficient was easily determined as $\varepsilon = 1100\,M^{-1}cm^{-1}$ [8]. The same radical in aqueous solution shows the same wavelength of maximum absorption band and a similar molar extinction value, but its lifetime is several orders of magnitude shorter. The possibilities of measuring ε has helped to estimate the value of S. Such indirect methods create possibilities to solve problems of molar extinction coefficient also in other systems.

Polymers investigated by the DRS method can be divided into two types according to the form in which they are subjected to investigation: (A) Powders, as obtained from the polymerization line, or prepared from sheets by liquid nitrogen freezing and mechanical disintegration, and (B) films, foils or blocks with a flat surface. The first group causes no difficulties in measurement, because powders unirradiated and irradiated have the same texture of identical optical properties, perfectly compensated in both beams of analytical light. The second group may cause some problems, when the smoothness of the surface of reference and irradiated sample differ even slightly. These slight differences can lead to bad reproducibility of measurements, due to the large impact of relation of intensity of specular and reflected light. For that case we have developed a new approach consisting of controlled mechanical roughening of the flat surfaces of both reference and irradiated samples. Such approach has brought closer the results on powders and films.

Looking for the best characterization of irradiated polymers, instrumental methods other than spectrophotometry are considered, *e.g.*, EPR spectrometry. The comparison of spectrophotometric results with EPR spectra shows additional advantage of the DRS method, because the optical spectrophotometry detects any species showing electronic spectra, whereas the EPR spectroscopy is limited to paramagnetic species, not necessarily surviving for a reasonable period of time in irradiated material. Another advantage is the positive role of investigation of rather shallow surface layer of the sample.

The information needed often at higher LET (Linear Energy Transfer) radiation effects (in radiation processing of surfaces) in a polymer systems, is easily supplied by DRS. Low range of high LET radiations is in our case of advantage, because most of the energy is deposited close to the surface, *i.e.*, in the layer "seen" preferably by the DRS.

4. RADIATION CHEMISTRY OF POLYMERS AND THEIR CONNECTION WITH THE DRS METHOD

Radiation chemistry of polymers is nowadays a large field in which all possible methods of measurement are applied for product analysis, from stable products of radiolysis to transient ones. The latter are sometimes stable enough to be investigated after days, and sometimes hours after irradiation. That is the case with DRS as well as with the electron paramagnetic resonance (EPR) using normal equipment, without turning to special equipment for time resolved investigations down to nanoseconds. Normal EPR instruments allow investigation of low temperature irradiated polymers, in which the secondary reactions of free radicals are slowed down. Extension of the life of free radicals by cooling must take into account the possibility not to go below the threshold of structural changes of the polymer what may introduce new conditions and create practically a new system. In the contrary to the EPR method, the DRS cannot be applied to deep frozen samples at the time being, with sufficient precision.

Several polymeric systems has been investigated for the radiation induced reactions. Usage of gamma radiation (5 kGy/h) was limited, because of slow supply of radiation energy, competing with the rate of diffusion of oxygen from the air. High power, high energy electron accelerators (10 or 13 MeV) were the principal sources of ionizing radiation, as described in [9]. As an example of our investigations let us analyze the radiolysis of virgin polypropylene with the application of both method – DRS and EPR (Bruker ESP 300 spectrometer was used) which could have been done at room temperature. Polypropylene (PP) belongs to the group of unstable polymers which cannot be processed and applied without additives. Investigations on radiation chemistry of stabilized PP is not conclusive because the response to the radiation induced effects is influenced by radiation chemistry of additives. The pristine PP cannot be processed into transparent samples without additives and therefore optical absorption spectra of powders had to be made by the DRS method. Papers [10,11] present first experiments with irradiated polypropylene powder, showing at the same time advantages of direct measurement of irradiated sample *vs.* unirradiated one, using double beam spectrophotometer with light integrating sphere.

Identification of the chromophoric groups created by radiation has been done by comparison with low MW peroxides (tertbutyl hydroperoxide and ditertbutylperoxide) and keton compounds (di-isopropylketon and di-isobutylketon) introduced into the matrix of the PP powder.

Decay of radiation induced (in the presence of oxygen) peroxides observed spectrophotometrically in the far UV in irradiated polypropylene was correlated with the decay of EPR signals (Figure 2). An example of the DRS record, showing the build up of ketonic moieties in irradiated polypropylene is shown in Figure 3.

Chain oxidation of irradiated PP exposed to air, proceeding for months was followed gravimetrically, that proved to be more convenient and precise in comparison to the manometric method. One can find in the literature descriptions of measurement of oxygen absorption consisting in the determination of oxygen pressure above the irradiated material (manometric method). We have found the pressure measuring method difficult to apply and of insufficient precision. The better method was gravimetric, realized with modern

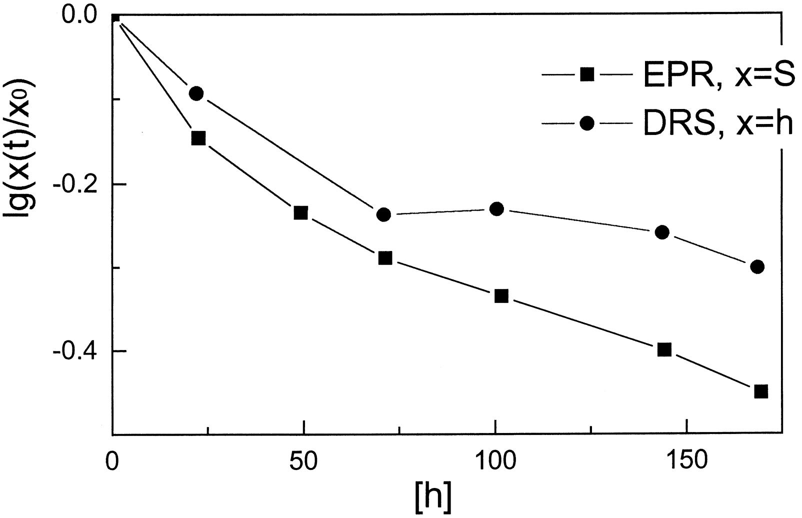

FIGURE 2 Comparison of decays of the EPR signal attributed to peroxides and decays of far-UV optical absorption as measured by the DRS in the function of time. At longer times, the far-UV absorption of peroxides is disturbed by the tail of ketonic groups absorption with maximum at the near-UV.

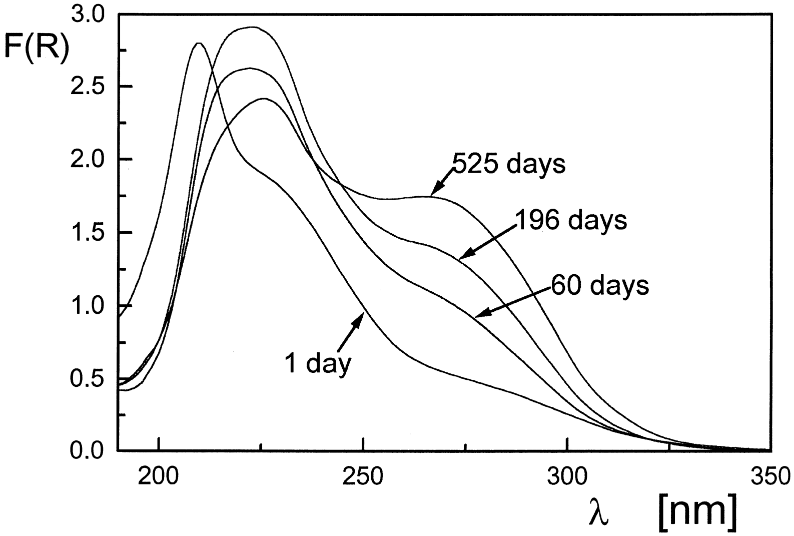

FIGURE 3 DRS records of optical absorption of irradiated polypropylene, exposed to air. The increase of absorption in the 260–280 nm band is attributed to keton groups in the polypropylene chain. Days after irradiation are indicated.

electronic balances of much better precision than old ones. Gravimetric method is superior in our case because of substantial increases of weight, reaching almost 1 mg per day and 20 g of polypropylene at the beginning of the oxidation process. The new approach offered free choice in adjusting the composition and pressure of gas above irradiated polypropylene.

The G value of oxygen absorption and formation of ketonic groups on polypropylene chains was up to 12 μ mol J^{-1}, depending on the dose and the time elapsed from irradiation. Once initiated, the reaction proceeds for months. Consumption of oxygen and formation of ketonic moieties are not influenced by the humidity of air. The advantage of the DRS method, working with high ε's in the UV, in comparison to the IR spectrophotometry, which was considered for measurement of ketonic groups, is that the latter demands higher concentrations, due to low molar extinction coefficients, common in the absorption in infrared region. Thus, the application of three completely different methods to recognize one complex of chemical reactions has given a full picture of the phenomena, well founded and self-consistent.

Another application of the DRS method to radiation chemistry, this time to the study of energy transfer in blends of polymers is described in the following paper by żuchowska, Zagórski, Przybytniak and Rafalski [12] presented in the POLYCHAR 8 Conference: "Influence of butadiene/styrene copolymers on the stabilization of propylene in electron beam irradiation". That paper shows, that DRS method is able to detect in that system chemical changes resulting from the reactions which start from single ionization spurs. The energy disturbance, of various origins travels to sites of energy sinks, in that case of SBS. The latter is present in 10% concentration only, and absorbing that proportion of ionizing radiation, but is more effective in the protection of polypropylene from the formation of unsaturations, than could have been expected. Free radicals observed in the EPR investigation are connected rather with multi-ionization spurs.

The DRS method is not limited to investigation of radiolysis of polymers and can be used also for investigations of stabilization in which irradiation is not involved. Low thermal stability of polypropylene without proper additives causes the occurrence of absorption spectra in the UV after simple heating, indicating the presence of unsaturations (Figure 4). The introductory experiment [13] shows how

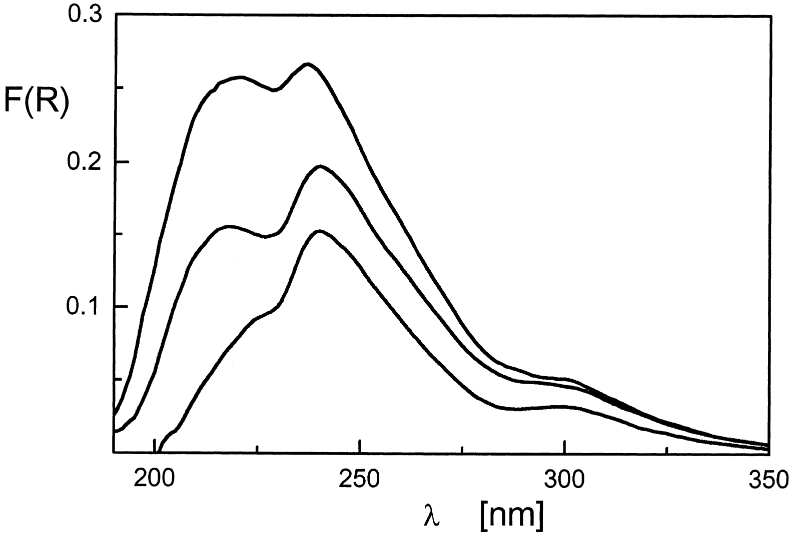

FIGURE 4 UV absorptions in pristine polypropylene after heating. Consecutive curves from top to the bottom were obtained on the same material: (top curve) PP powder taken from the container under argon, (middle curve) material aerated for two weeks, (bottom curve) material aerated for one month. All samples heated for 2 h at 110°C. Reference – unheated samples of the same material (13).

unstable virgin polypropylene is, as the room temperature exposure to air of the polymer, changes its response to heating. Research involving the DRS method is continuing not only on radiolysis of polymers, but also on thermal stabilization of polypropylene and its blends.

5. CONCLUSIONS

The diffuse reflected light spectrophotometry proved its usefulness in the investigation of radiation chemistry of polymers, being sometimes a key method among other methods of investigation. In combination with other methods of investigation, like EPR, it helps to detect the participation of single- and multi-ionization spurs in radiolysis of polymers [14].

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