Applying of spectroscopic methods in the investigation of radical polymerization processes and products

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Introduction

The application of some supplementary spectroscopic methods, i.e. infrared (IR) and ultraviolet-visible (UV-VIS) spectroscopy or nuclear magnetic resonance (NMR), allows receiving the necessary information to identify the chemical structure of compounds and moreover the investigation of various processes, e.g. in polymer chemistry: starting from initiator synthesis, their behaviour at various conditions, through the other polymerization substrates, following products study, and also investigations of other processes – polymers modification or destruction. The examples of such studies are illustrated in the present work.

The process investigation through substrates and products analysis

The spectroscopic methods were applied to characterize azoinitiators used in the radical polymerization of vinyl monomers. Azoester initiators were received in Pinner’s reaction of 2,2’-azoisobutyronitrile (AIBN) and homological series of monodisperse diols: 1,4-butanediol (1,4-BD), tri(oxyethylene)diol [Tri(OE)D], tetra(oxyethylene)diol [Tetra(OE)D] and also polydisperse oligo(oxyethylene)diols with $M_n = 200$ or $400\,\text{g/mol}$ [OOED(200) or OOED(400)]. The chemical structure and quantitative molecular analysis were determined, among other things, by proton magnetic resonance spectroscopy ($^1\text{H NMR}$). Thanks to the $^1\text{H NMR}$ method it was possible to establish which particles from polydisperse diol OOED(400) were incorporated into the AIB-OOE(400) azoester. The example of the investigation is shown in Figure 1 [1].

The UV-VIS spectroscopy can be successfully used in the kinetic study of thermal decomposition of azoinitiators [2]. The UV-VIS spectra of both 2,2’-azoisobutyronitrile (AIBN) and the other initiators studied, e.g. 2,2’-azobis (2-methyl-4-hydroxybutyl) propionate (AIB-BD), include the symmetrical absorption band assigned to azo-bond at $\lambda_{max} = 344.7\,\text{nm}$ and $361.7\,\text{nm}$, respectively (Fig. 2). Maximum of the band characteristic for the azo-bond is shifted into the longer wave’s direction (relating to initiators being the derivatives of AIBN) because of the interaction of the longer chains from diols in the vicinity of azo-bond. During the thermal decomposition reaction progress the second band appears (in the case of AIBN at $\lambda_{max} = 290\,\text{nm}$), which at first increases (absorbance grows) and then decreases. The presence of additional band results from the formation of intermediate products of the initiator thermal decomposition. The influence of the intermediate products on the shape of the UV-VIS spectrum is especially visible in the case of AIBN (Fig. 2a). For AIB-BD and other initiators studied the additional band disturbs to the considerably lesser extend the course of absorption spectrum (Fig. 2b). Besides their intensities suggest different from AIBN, more homogenous decomposition to intermediate products.

Fig. 1. $^1\text{H NMR}$ spectra of OOED(400) and AIBN (synthesis substrates), and AIB-OOE(400) azoester (product) [1]

Fig. 2. The dependence of absorbance (A) on the wavelength (UV-VIS) during the thermal decomposition of azoinitiators in DMF solution at 75°C (decomposition period from 0 to 1050 minutes): a – 2,2’-azoisobutyronitrile (AIBN); b – 2,2’-azobis(2-methyl-4-hydroxybutyl) propionate (AIB-BD) [1, 2]
The connection of FTIR spectroscopy and thermogravimetric analysis (TGA) allows to e.g. the study of thermal destruction processes of polymers [3]. The example of such investigation and results distinctive for the TGA-FTIR method are showed in Figure 3.

The products of thermal destruction of poly(methyl methacrylate) (PMMA) and the composite with single wall carbon nanotubes (PMMA/SWCNT) with various SWCNT content were identified by the FTIR method in the range of 800 - 2000 cm\(^{-1}\), among them the main depolymerization product – monomer associated with 1170 cm\(^{-1}\). The depolymerization process was ended after 1500 s in the temperature of 495°C with ashing of the residue, which amount was associated with the amount of SWCNT added in the polymerization in situ process.

The products analysis

The azoesters with chemical structure changing with dependence on diol used in their synthesis are the products of Pinner's reaction, as mentioned earlier. The influence of the diol chain length is visible in the absorption spectra (UV-VIS) of the azoinitiators (Fig. 4) [1].

The maximum of the band confirming the presence of azo-bond for AlBN is assigned to the wave number \(\lambda_{max} = 344.6\) nm, whereas for azoesters, together with increase of the length of diol chain built in, the maxima are shifted to the higher values of wavelength. This is known as the bathochromic effect.

The study of products of the polymerization in situ with carbon nanoparticles in the form of carbon nanotubes SWCNT or fullerenes \(C_{60}\), with application of IR and UV-VIS spectroscopic methods, allows to distinguish physical and chemical effects in the intermolecular interactions [4, 5]. The example of the study is illustrated in Figure 5 and 6.

The UV-VIS spectra in Figure 5 confirm the chemical bonding of fullerenes with PMMA, the \(C_{60}\) bands are sharply outlined and their intensity depends on the amount of fullerenes in the polymer.

The IR spectrum of poly(methyl methacrylate) with carbon nanotubes (Fig. 6) shows the splitting of the C=O band in ester group, which may result from the fact that a part of mers are in the vicinity not of the next identical mer but with chemical bonded carbon nanoparticle.

Whereas in the spectrum of polystyrene with participation of SWCNT the relative intensity of signal at 700 cm\(^{-1}\) for CAr–H oscillation increases which is the result of interactions with nanotubes built also with six-membered rings.
Literature


Translation into English by the Author

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