Polymers
Polymerization and Degradation Monitored by EPR

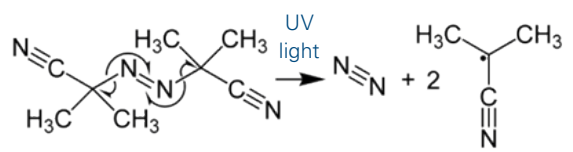
The degradation of polymers due to light exposure leads to discoloration of the polymer and a decrease in the mechanical properties (elasticity, toughness, etc). To prevent this decomposition, light stabilizers are added to the polymer. By monitoring the EPR signals of these light stabilizer, their effectiveness can be evaluated using the Magnettech ESR5000.

Introduction

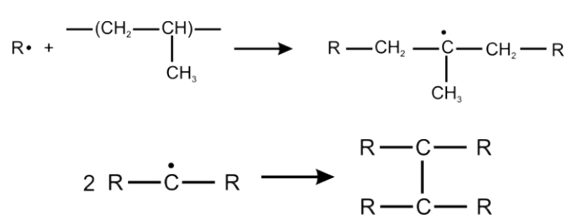
In polymers, radical reactions are involved in the various processes such as polymerization, cross-linking and degradation. It is possible to investigate these phenomena by using EPR spectroscopy. These methods are used in both academic and industrial settings for research and quality control.

EPR is an important tool to study different polymerization reactions such as:

- Photo initiation and radical formation upon laser irradiation



- Polymerization reaction kinetics
- Cross-linking reactions



- Photo degradation analysis
- Inhibition effect of Hindered Amine Light Stabilizers (HALS) on UV degradation of polymers

Challenge

A wide range of reactions occur in polymers due to thermal and light activated mechanisms. These reactions are dominated by free radicals and influence both the creation and the destruction of the polymer.

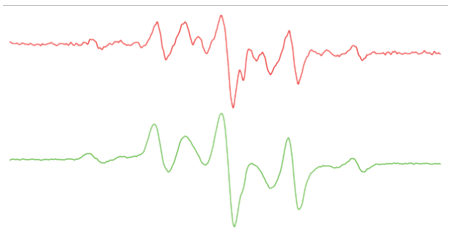
Solution

Direct detection of the free radicals present in polymers during thermal or light treatment offers insight into the effective control of polymer formation and degradation.

Equipment

The Magnettech ESR5000 UV-Vis irradiation system and variable temperature system provide the ability to monitor free radicals during in-situ irradiation and thermalization of the sample of interest within the microwave cavity. The UV-Vis system features an integrated light source with holder for precise positioning to guide the UV-Vis light to the sample cavity interface thus assuring high light transmission efficiency and compliance with international safety standards.

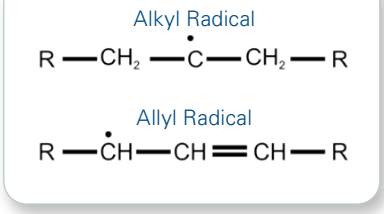
The integrated light source allows UV-Vis irradiation at specific wavelengths and is directly operated by ESRStudio software. Another optional and external UV-Vis irradiation can provide irradiation at broader wavelength regions. The variable temperature system uses an inert transfer gas to heat the sample to temperatures up to 473 K. In addition, a high temperature controller provides sample treatment up to 723 K.

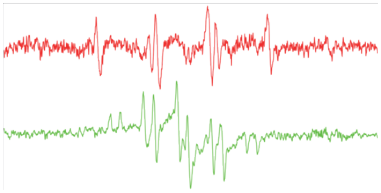


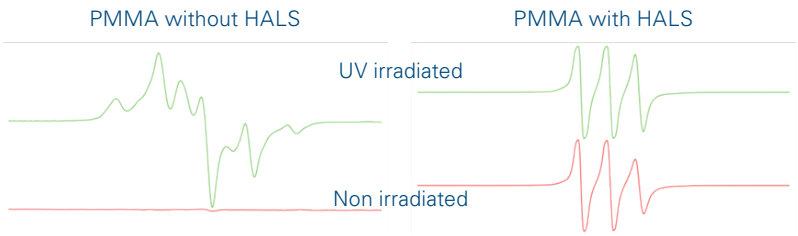
- The polymerization reaction of MMA (Methyl-Methacrylate) mixed with initiator AIBN (Azobisisobutyronitrile) at 50 °C during UV irradiation is monitored using the ESR5000.

- Snapshots from a kinetics experiment showing the evolution of the radicals formed during UV irradiation at 4 min (top) and 8 min (bottom).

- Polyethylene (PE) in the presence of the cross-linking agent DCP (Dicumyl peroxide) forms two types of C-centered radicals while heating at 150 °C.
- At early times during the heating, an Alkyl radical is formed (top) and after long term heating an Allyl radical is formed (bottom).
- SpinCount uses the double integral value of the EPR spectrum to calculate the concentration of the PE radicals formed over time.







- The effectiveness of light stabilizers (HALS) for preventing polymer degradation by UV irradiation is easily evaluated with the ESR5000.
- The EPR signal generated in the polymer during UV irradiation (left) is completely suppressed after addition of the HALS stabilizer where only the HALS EPR spectrum is observed (right).

Key Features include:

- Easy-to-use ESRStudio software
- Kinetics experiments allow the showing of formation of polymer radicals
- SpinCount module to quantify the total number of spins and to determine the radical concentration
- The integrated UV-Vis irradiation system (400 mW, wavelengths 365, 462, 523, 590, 625, and 850 nm) enables in-situ irradiation of the sample in the microwave cavity
- The external UV-Vis irradiation system (up to 200 W Hg-Xe lamp) allows irradiation in the UVA-, UVB-, Vis-, or UV-Vis regions. Both systems are fully controlled by the ESRStudio software

References for further reading

1. Peng J.S., Ming L.-J., Lin Y.-S., Lee S. EPR study of radical annihilation kinetics of γ-ray-irradiated acrylic (PMMA) at elevated temperatures, Polymer (2011) 52(26) 6090
2. De Cooman H., Desmet T., Callens F., Dubruel P. Role of radicals in UV-initiated postplasma grafting of poly-ε-caprolactone: an electron paramagnetic resonance study, J. Pol. Sci. Part A (2012) 50(11) 2142
3. Kasser M.J., Silverman J., Al-Sheikhly M. EPR simulation of polyenyl radicals in ultrahigh molecular weight polyethylene, Macromolecules (2010) 43(21) 8862

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