Spectroscopic Methods Studies in Polymer

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ABSTRACT

The physico – chemical changes induced in polymers following to radiation can be studied by a range of spectroscopic techniques. Recent developments in instrumentation and data analysis procedures in electronic, vibrational and magnetic resonance spectroscopes have provided considerable new insights, into polymer structure and behavior. The applications of these spectroscopic methods in polymer studies are reviewed with emphasis on their utility in investigations of radiation effects on macromolecules.

Keywords: ESCA; polymer; Fluorescence spectra; Excitation wavelength

1. INTRODUCTION

Spectroscopic methods are new widely used in the polymer field as an analytical to probe structure and to obtain information on physico-chemical changes occurring in polymers and polymer additives. Spectroscopy utilizes the interaction of radiation with matter to provide details of molecular energy levels, energy state lifetimes and transition probabilities for polymers.

This information in turn, may be applied in studying chemical structure, molecular environment, polymer tacticity, conformation, and to monitor changes in these properties following external perturbations (e.g., mechanical stress, thermal treatment, radiation exposure).

The advantages of spectroscopic measurements over other means of polymer characterization that they are a non-destructive and rapid means of providing information at a molecular level (1). Exposure of polymers to ultraviolet and higher energy radiation can lead to extensive physical and chemical modification of polymeric materials. These changes in properties may have both detrimental and beneficial consequences in determining the end-uses of the polymer Spectroscopy can provide a detailed insight into the mechanisms of polymer modification occurring under irradiation thus enabling control of the final material properties (1).

There are several well written texts describing the theory and application of spectroscopy to polymer system some aspects relevant to radiation effects polymeric materials are reviewed with particular emphasis on new developments in instrumentation (1). The various spectroscopic methods can be distinguished by the energy of the transitions investigated (c.f. Figure 1) and this notation is employed in the sub-headings discussed below (1). Surface analysis techniques will not be described in detail in this article although mention may be made of ESCA (Electron Spectroscopy for Chemical Analysis) as one recent technique which may be used to analyze surface properties.

ESCA monitors the kinetic energy of electron detached from e sample following irradiation with an X-ray source (1). The detached electrons arise from atoms an molecules at the surface of the polymer (~2 nm depth) an thus information concerning chemical modifications (e.g. photo-oxidation) at surfaces can be obtained (1).

2. EXPERIMENTAL

The absorption and emission of radiation in the near ultraviolet (UV) and visible regions of the electromagnetic spectrum are associated with electronic (and associated vibronic) transitions involving π- and/or n-electron systems of molecules. Synthetic and natural polymers absorb in the UV region and particularly strong A absorption spectra are recorded for polymers containing aromatic and heteroaromatic groups (e.g., poly(styrenes), poly(vinyl naphthalenes), poly(vinyl carbazoles) polymers with chromophores exhibiting nπ* transitions (e.g., C=O) exhibit weaker UV-absorption and these groups together with unsaturated carbon-carbon bonds which develop during radiation damage can be detected by electronic absorption spectroscopy (2).

The absorption and emission processes occurring in organic molecules including polymers can be discussed qualitatively with reference to the state diagram of Jablonskii (Figure 2). Absorption of radiation by the molecule leads to promotion of an electron from the ground singlet state (So) to a higher electronic state which, through conservation of spin, will also be a singlet state (Sn).

The energies of radiation required to promote e1ectrons to higher energy states and the range of associated vibrational energy levels, results in the recorded absorption spectrum with the intensity distribution of the spectrum reflecting the relative probabilities of the transitions. Associated with each excited singlet state there is an electronic state of lower energy in which the electron spins are parallel, the triplet state. It should be noted that absorption spectra arising from any excited state of the molecule (e.g., S_1 S_n absorption, T_1 - T_n absorption) or other transient (2).
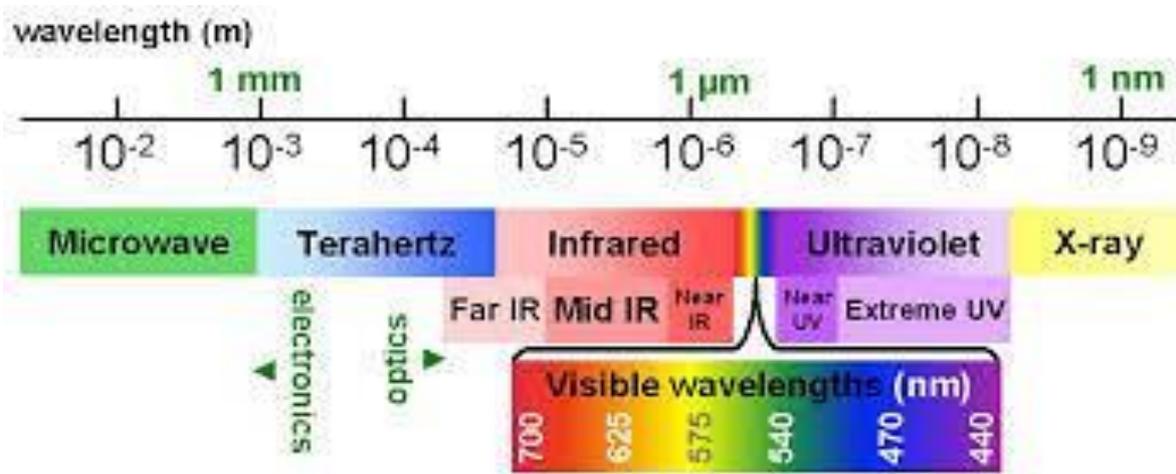
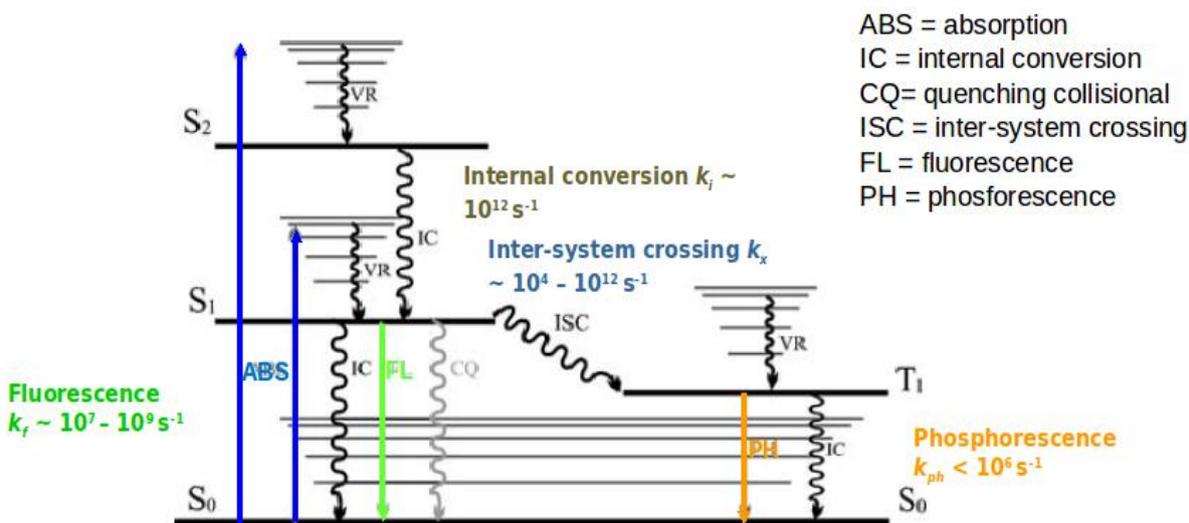**Figure 1.** Spectral range of spectroscopic techniques.

Figure 2. Jablonskii diagram.

The possible fate of excitation energy residing in molecules is also shown in Figure 2. The relaxation of the electron to the initial ground state and accompanying emission of radiation results in the fluoresce spectrum (S1 - So) or phosphorescence spectrum (T1 - So). In addition to the radiative processes, non-radiative photophysical and photochemical processes can also occur. Internal conversion and intersystem crossing are the non-radiative photophysical processes between electronic states of the same spin multiplicity and different spin multiplicities respectively.

The lifetime of the excited state will be influenced by the relative magnitudes of these non-radiative processes and thus time-resolved spectroscopy can provide information on the dynamics of excited state depletion mechanisms, e.g.

	Process	Rate
$S_0 + hv \rightarrow S_1$	Absorption	I_a
$S_1 \rightarrow S_0^{\cdot} + hv_F$	Fluorescence	K_F
$S_1 \rightarrow S_0$	Internal conversion	K_{IC}
$S_1 \rightarrow T_1$	Intersystem crossing	K_{ISC}
$S_1 \rightarrow$ products	Reaction	K_R

$$\tau_F = (K_F + K_{IC} + K_{ISC} + K_R)^{-1}$$

The lifetime of the Singlet excited state (the fluorescence lifetime τ_F) is the order of picoseconds to 100 nanoseconds (10^{-12}- 10^{-7} seconds) and can now be measured accurately using pulsed laser excitation methods and other techniques. Since the radiative transition the lowest triplet state to the ground state is formally forbidden by selection rules. The phosphorescence lifetimes fan be longer, of the order of seconds.

3. RESULTS AND DISCUSSION

The UV visible absorption and emission spectra and excited state lifetimes of polymers are sensitive to chemical structure, polymer conformation and molecular environment and thus information concerning these properties is accessible by electronic spectroscopy measurements (4-6). One example of the application of such measurements is given in Figure 3 which illustrates the possible energy dissipation pathways which can occur in a polymer containing aromatic side groups following absorption of radiation.

From dilute solutions of poly (styrene) (PS) and a 1:1 alternating copolymer of styrene and maleic anhydride are shown. For PS, fluorescence from the excited aromatic phenyl chromophores is observed (fluorescence maximum 290 nm) together with a broad emission from excimer sites in the polymer (fluorescence maximum 330 nm). However in the alternating copolymer no excimer fluorescence is detected demonstrating that under these conditions excimer energy trap sites in PS must form between adjacent phenyl group chromophores along the polymer chain.

Recent developments and fast detection methods now allow the kinetic behaviour of the excited state species arising from absorption of radiation by polymers to be studied on time-scales down to the picosecond region (5). An example of a time-resolved fluorescence spectrometer which can be used to study such ultrafast phenomena is illustrated in Figure 5 (7).

The commercially available laser source is a mode locked argon-ion, laser synchronously pumping a cavity dumped dye laser. This laser system produces tunable light pulses, each pulse with a time duration of about 10 picoseconds and with pulse repetition rates up to 80 million laser pulses/second. The laser pulses are used to excite the sample under the study and the resulting sample fluorescence is spectrally dispersed through a monochromator and detected by a fast photomultiplier tube (or in some cases a streak camera (5).

In the time-correlated single photon counting technique depicted in Figure 5, electronic pulses synchronised with the laser pulses are used to initia voltage-time ramp in the time-to-amplitude converter (TAC). while electronic pulses arising from fluorescence photons incident on the photomultiplier tube terminate the voltage ramp.

The amplitude of the voltage pulse from the TAC, which is stored in a memory of a multichannel analyser operating in pulse height analysis mode, will be directly rebated to the time between excitation of the sample by the laser pulse and the detection of a fluorescence photon. Collection of many such events at a fixed emission wavelength results in a fluorescence decay curve which may be analyzed to extract fluorescence decay parameters (5), Alternatively accumulation of fluorescence events at a number of emission wavelengths and at various times after excitation can produce three-dimensional hyper-surfaces displaying the spectral, temporal and intensity information simultaneously (Figure 5).
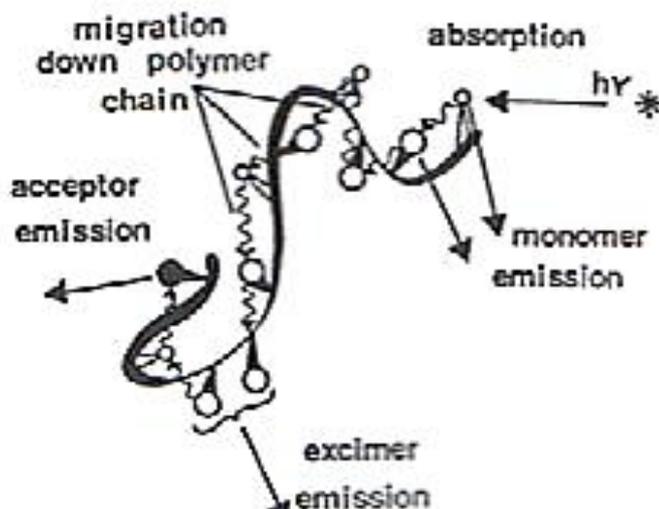

Figure 3. Energy relaxation pathways in a polymer containing aromatic side groups following absorption of light. (Reproduced with permission from (21).
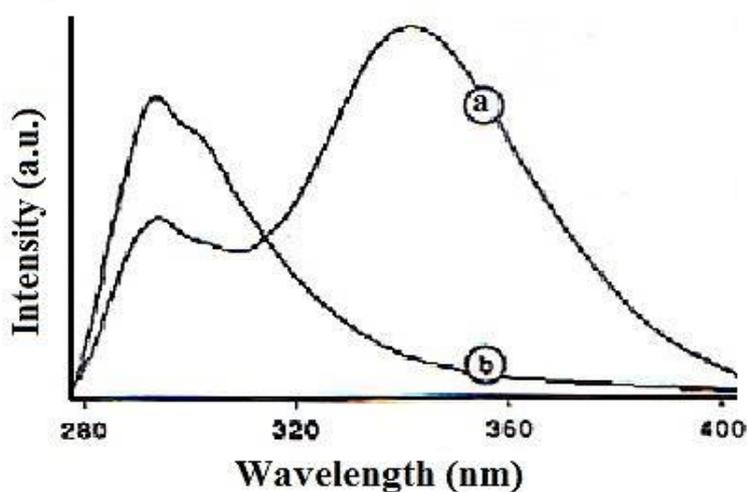

Figure 4. Fluorescence spectra of (a) polystyrene) and (b) tyrene/malefic anhydride alternating copolymer in Tetrahydrofuran at 20 °C. λ_{ex}: 265nm.
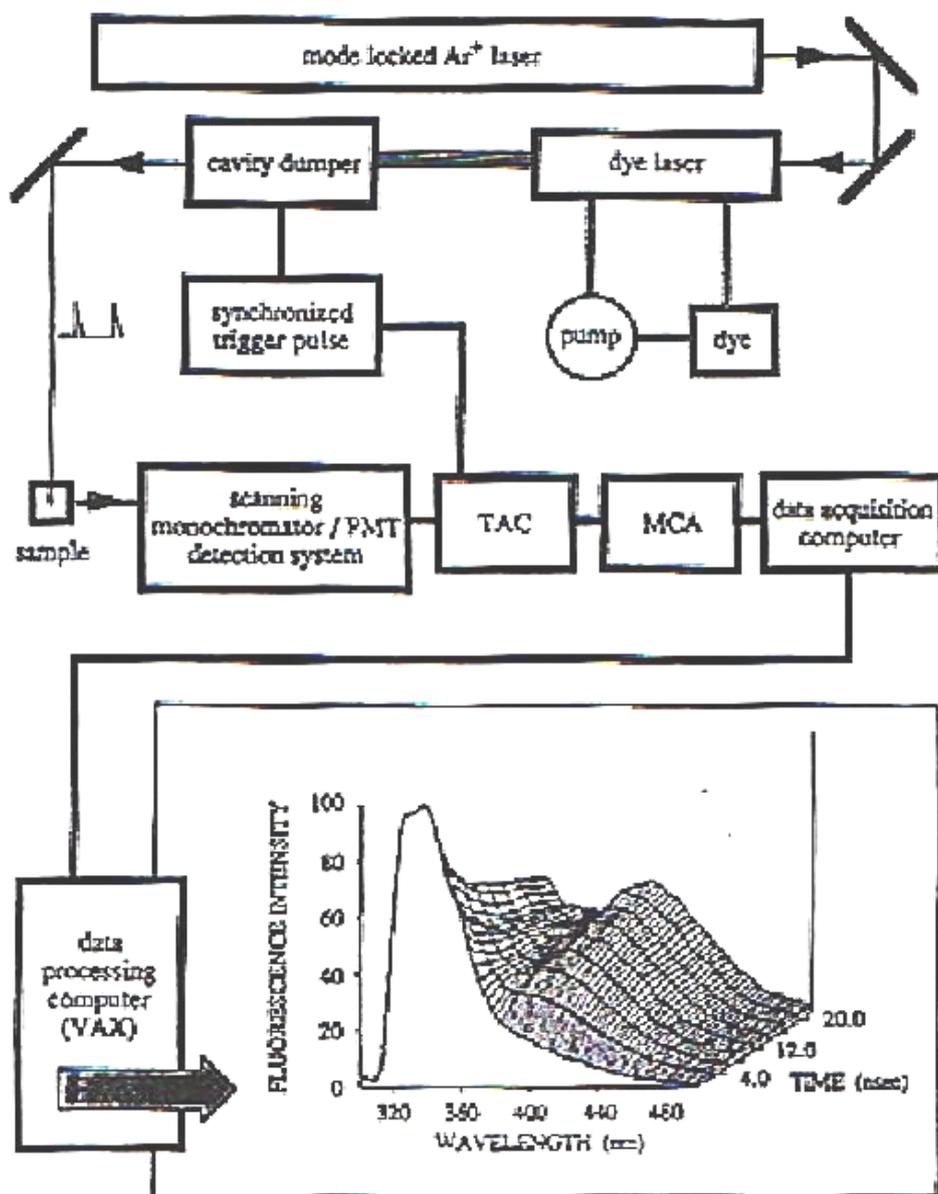
Figure 5. Schematic diagram of a time –resolved fluorescence spectrometer using a picosecond laser as an excitation source. Inset diagram: intensity /time/wavelength surface for poly (acenaphthalene) in benzene at 20 °C. Excitation wavelength 295nm (21)

Be analyzed to extract fluorescence decay parameters (5), Alternatively accumulation of fluorescence events at a number of emission wavelengths and at various times after excitation can produce three-dimensional hyper surfaces displaying the spectral, temporal and intensity information simultaneously (Figure 5).

The inset diagram in Figure 5 depicts the kinetic behaviour of fluorescence from single excited chromophores (fluorescence maximum 340 nm) and excimer sites (fluorescence maximum 400 nm) following excitation of a solution of poly(acenaph halen) with laser pulses at 295 nm. Such hypersurfaces provide an overview of the excited state processes according in polymers following irradiation and can show here the energy initially absorbed by the polymer finally resides and the rates of various energy dissipation pathways. Absorption, fluorescence and phosphorescence measurements have been applied to the study of radiation effects on a wide range of polymers and polymer additives (1,7). Chemiluminescence is a further example of the application of electronic spectroscopy measurements to polymer degradation studies. The weak visible radiation emitted from polymers undergoing thermo-oxidative degradation has been attributed to emission from electronically excited oxidation products and thus Chemiluminescence provides a means of detecting and monitoring the incipient stages of certain polymer decomposition, processes (1,7).

A quantum description of the stretching and bending vibrations of molecular bonds results in the assignment of vibrational energy levels associated with each electronic state of functional groups in polymers (1,). Since bond force constants and atomic masses determine the vibrationa' frequencies, the energy levels will be characteristic of the chemical groups present in the polymer. Transitions between these vibrational energy levels can be investigated using infrared and Raman spectroscopies.
Infrared (IR~ spectroscopy has been widely used in polymer studies for the assignment of molecular structure and for monitoring changes in the arrangement of chemical bonds

Information concerning conformation, tacticity and crystallinity may also be obtained (1). Vibrational transitions accesssible to IR spectroscopy are governed by the selection rule that there must be a change in dipole moment during excitation of the polymer vibrations. Thus symmetric vibrations which are detected by Raman spectroscopy are inaccessible to IR absorption measurements. Polar groups, such as carbonyl (C=O) and hydroxyl (OH), have a strong ground state dipole moment and show strong IR absorptions at characteristic frequencies .aThe IR spectrum can thus be used as a 'fingerprint of molecular structure and, since the positions of vibrational frequencies are sensitive to neighboring chemical groups, conclusions concerning local environment can be made. A considerable volume of polymer IR spectra have been recorded and published (12).

Both conventional dispersive element IR spectrometers and Fourier Transform infrared (FTIR) interferometer based instruments are available to record IR spectra o polymers. In the conventional instruments a dispersive element, such as a grating or prism is used to measure the frequencies at which infrared radiation is absorbed by the sample. An interferometer (Figure 6) constitutes the basis of the FTIR instrument. In the interferometer the IR radiation is split into two paths and, after reflection from mirrors (one movable), the beams are recombined at the beam splitter.

When the path lengths followed by the two beams are identical all wavelengths of radiation incident on the beam splitter add coherently and result in the maximum flux at the detector. At other positions of the movable mirror destructive interference of each wavelength at the beam splitter occurs an the flux at the detector will decrease. The interferogram F(x)) produced by recording the radiation flux as the mirror undergoes translational movement has the form of a damped oscillation corresponding to:

$$F(x) = \int A(v) \cos(2\pi v) \, dv \qquad \text{..... [1]}$$

where A (v) is the spectral intensity distribution containing the spectroscopic information.

The spectroscopic data is extracted by a Fourier transform of the interferogram (11). Tfie' instrument is single beam and a blank must also be measured and subsequently subtracted. A computer carries out the Fourier transform calculations, performs various control functions and manipulates the ' data for display and interpretation.

FTIR instruments offer advantages in speed and higher signal –to- noise ratios compared to dispersive IR spectrometers. These advantages combined with the facility for extensive data processing had seen the FTIR technique find increasing applications in polymer studies (11).

IR spectroscopy has proved most useful in studying chemical modifications of polymer induced by external factors including radiation damage (1,13). Oxidation is an important degradation-pattway following exposure to both heat and radiation. The strongly polar functional groups which are the products of oxidative damage (e.g., OH, C=O) are readily detected by IR spectroscopy and thus this technique can be used to follow the early stages of degradation. Attenuated total reflection (ATR) of IR radiation (1) may a1so used to monitor surface modifications during degradation.

An example of the application of IR spectroscopy is in the photooxidation on of poly(propylene) (1,3). During the early stages of oxidation absorption due to aldehydes. (1735 cm^{-1}) and ketones (1720 cm^{-1}) are apparent while at later times carboxylic acids (1710 cm^{-1}) can be detected.

In poly (ethylene) hydroperoxides (3550 cm^{-1}) are observed during early stages of irradiation while FTIR has revealed an increase in vinyl end groups, carbonyls and trans-vinylidene double bonds (11) Correlations have been noted between physical changes in the polymer and chain scission processes detected by IR spectroscopy during photo degradation of poly (ethylene).

The advent of 1a'sers has assisted in the development of Raman spectroscopy as a means of recording vibrational spectra of polymers and other molecular systems. Raman spectroscopy is based on inelastic light scattering and uses monochromatic radiation in the visible region as the excitation source. Analysis of radiation scattered from a sample of molecules indicates the presence of frequencies which are spectrally shifted to lower energies (Stokes lines) and higher energies (anti-Stokes lines) compared to the incident radiation. The spectrally shifted lines arise due to the transfer of vibrational quanta between the interacting radiation and the medium. The observed transitions are governed by the selection rul that there is a change in polarizability during the molecular vibration and thus IR-inactive totally symmetric vibrations may be observed. In order to discriminate the Raman spectral lines from the strong Tyndall scattering of the incident radiation, highly monochromatic radiation available from laser sources (typically argon-ion or krypton lasers) is preferred and double or triple monochromators are often required to achieve the necessary spectral resolution. Resonance Raman scattering may also be observed if the frequency of the exciting radiation corresponds closely to an electronic absorption bond. In this case, the Raman lines arising from coupling of the vibrations with the electronic transition are much stronger than ordinary Raman scattering:

Further details of the theory and application of Raman spectroscopy in polymer studies can be found elsewhere (1,9). However, vibrational frequencies of functional groups in polymers can be characterized from the spacing of the Raman lines and thus information complementary to IR absorption spectroscopy can be obtained. In addition, since visible-

radiation is used the technique can be applied to aqueous media in contrast to IR spectroscopy, allowing studies of synthetic polyelectrolytes and biopolymers to be undertaken. Conformation and crystallinity of polymers have also been shown to influence the Raman spectra (1) while the possibility of studying scattering from small sample volumes in the focussed laser beam (~100 μm diameter), Can experiments excited states and transient species are produced during excitation of the sample by a short laser pulse. The Raman scattering induced by a second probe pulse incident on the sample after a fixed time delay can be used to characterize the vibrational frequencies and hence the structure of the intermediate species. The application of mode-locked tunable dye lasers has allowed the technique to be extended down to the picosecond time region. Transient species produced following absorption of picosecond light pulses by bacteriorhodopsin (a protein complex containing the retinal chromophore in the purple membrane of Halobacterium Halobium) have recently been undertaken. although the application of such measurements to synthetic macromolecular systems has yet to be fully investigated.

Electrons and nuclei have a magnetic moment associated with angular moment of the particles. In the presence of a magnetic field the degeneracy of discrete energy levels associated with the magnetic moment is removed and absorption and emission of radiation between these energy levels may be observed. The energy difference between the quantized levels depends on the magnetic field strength and is given by(17):

$$\Delta E = h\nu = g\mu B \qquad \ldots\ldots [2]$$

where g is a constant ($g_e = 2$ for free electrons; $g_N = 0.1$ to 6 for many nuclei, e.g., $g_N = 5.5854$ for a proton), μ is the bohr magneton (μ_B) for nuclei and B is the magnetic field flux density.

The technique of studying the absorption of radiation by unpaired electronics in a magnetic field called Electron spin – resonance (ERS) spectroscopy while the study of the resonance frequencies for nuclei is classified as Nuclear Magnetic field Resonance (NMR).

Spectroscopy under external magnetic field strengths of about 1 Tesla, ESR spectroscopy requires energies in the, microwave region (~10 GHz) to initiate transitions, since the interaction between nuclei and the magnetic field is much weaker, the NMR technique uses lower energy radio waves in the 1 to 5 meter hand.

Experimentally the sample is placed in a strong magnetic field and, rather than the frequency being scanned at constant field strength to detect absorption of radiation, in practice the frequency of exciting radiation is kept constant and the magnetic field flux is varied. Both ESR and NMR spectroscopy have found widespread application in polymer studies and several excellent texts describing the techniques are available (1,17,19).

FSR (Fourier spectroscopy resonance) spectroscopy requires the presence of unpaired electrons in the sample and thus it finds application in the study of triplet excited states, neutral free radicals and radical ions which may be formed in polymers following exposure to radiation. The degenerate energy levels of unpaired electrons are split into two lines in the presence of a magnetic field and single resonance absorption might be expected. However, there are often interactions between the magnetic moments of other neighboring nuclei (e.g., protons) and the electron leading to hyperfine splitting in the absorption spectrum (17). In this case, the electron and nuclear spins interact and impose slightly different energy levels on the original energy splitting arising from the effect of the magnetic field on the electron. Thus different resonant frequencies will be observed and the number and intensity of the absorption

bands in the spectrum can provide information about the chemical environment of the unpaired electron (1,13).

For example, poly (methyl methacrylate) exposed to high energy or UV radiation gives a nine line ESR spectrum, as depicted in Figure 7. Analysis of this spectrum has indicated that the likely structure of the free radical responsible is (11).

$$\sim CH_2- C^*(CH_3)COOCH_3$$

In poly (olefines) the metastable allyl radical is often observe by techniques following irradiation:

$$- CH_2- CH = CH\text{-}HC'\text{-} CH_2-$$

The capability to detect such species by ESR spectroscopy provides a means to analyses the mechanisms of polymer breakdown under irradiation (17,19) In addition, certain compounds used to photo stabilize polymers against UV radiation act by scavenging the reactive radicals to form more stable radical species (e.g., hindered phenoxy radicals) and thus the performance of these stabilizers can be assessed by ESR methods(17).

The species present in polymers that can be studied by SER are often highly reactive, short-lived and are present in low concentrations. However, developments in instrumentation have offered improvements in sensitivity and, combined with more reliable interpretation of data (1), the increasing application of this method of polymer characterization in studying radiation effects on polymers can be expected.

In contrast to ESR spectroscopy, which can only be used to study species with unpaired electrons, spectroscopy is applicable to the investigation of all polymer samples, Nuclei with non –zero total nuclear spin (e.g ^1H, ^{19}C, ^{13}F, ^{14}N will have a magnetic moment which will inter act with an external magnetic field resulting in quantized energy levels transition between these energy level s from the basis of NMR spectroscopy ^3H and C^{13}.

Table 1. Information from Spectroscopic Methods

| Spectroscopic Technique	Information Available
Electronic	Chromophore composition,
(Absorption, Fluorescence, phosphorescence)	Conformation, excited state behaviour, polymer mobility
Vibrational (IR, Raman)	Chemical structure , tacticity , conformation, chemical modification
Magnetic resonance (ESR, NMR)	Chemical structure , tacticity , conformation, polymer mobility (NMR); Radical , triplet state structure and behaviour (ESR).
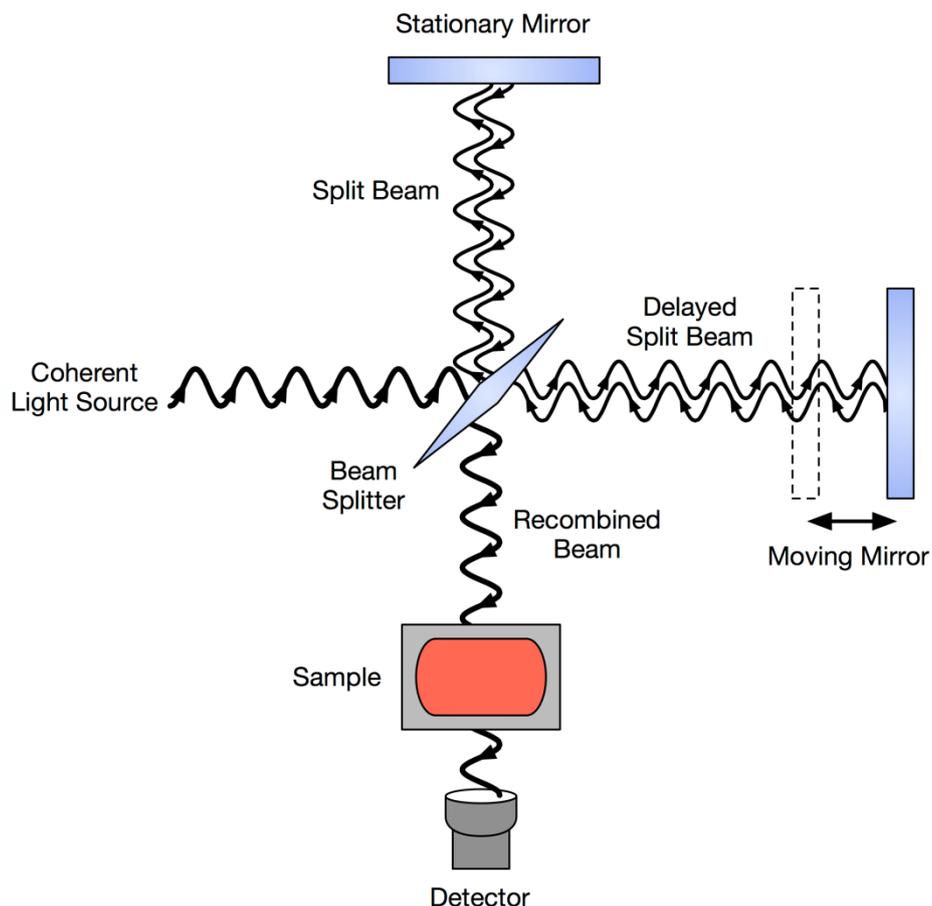
Figure 6. Schematic diagram of an interferometer as used in FTIR instruments (13).
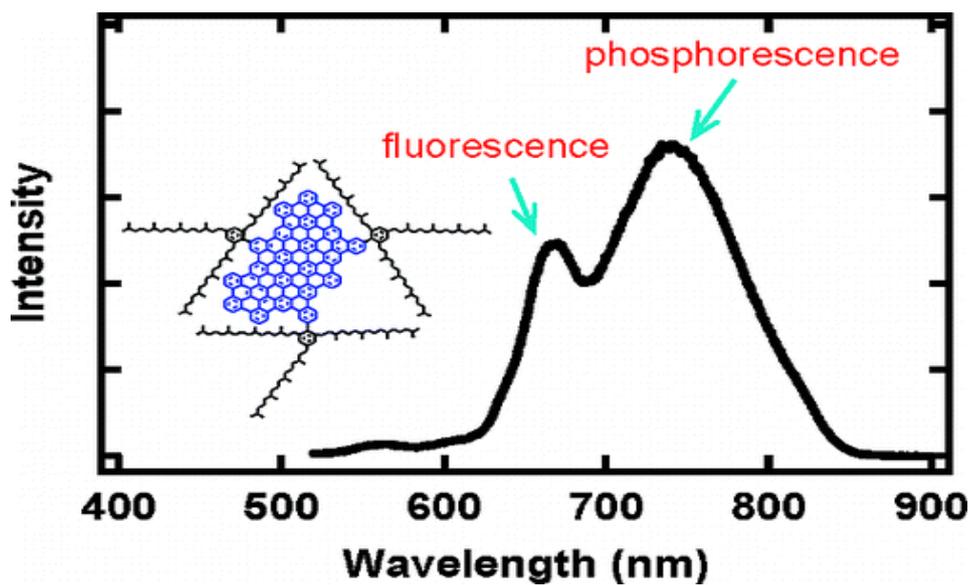

Figure 7. Form of ESR spectrum following irradiation of poly (methyl methacrylate) at room temperature (after 13) (Reproduced with permission (13).

Nuclei are the most useful nuclei in polymers for study by NMR methods (1).

The value of the magnetic field strength at which resonances occur for a particular nuclei is influenced by the chemical environment. The shift in absorption peaks in NMR spectra arise because the nuclei are shielded from the external field to differing extents by the diamagnetic behavior of surrounding molecular electrons. The 'chemical shift' of various resonance peaks can thus aid identification of the functional group *containing* the nuclei. In addition, hyperfine splittings of the peaks are observed which may be attributed to interactions between magnetic nuclei in different parts of the molecule. Analysis of the hyperfine splitting structure can thus provide additional information concerning the local chemical structure. A detailed discussion of the analysis of spectra is beyond the scope of this work and the reader is referred elsewhere for further descriptions (16,18). The spectra Obtained from polymers can be quite complicated, although ^{1}H NMR spectra can provide important information including details of polymer tacticity (1). The introduction of additional techniques such as pulsed Fourier Transform NMR has considerably increased the sensitivity of the method, allowing many magnetic nuclei which may be in low abundance, including ^{13}C, to be studied. The additional data available from these methods allow information on polymer structure, conformation and relaxation behaviour to be obtained (1.18,20). In respect of radiation effects in polymers, the primary application of NMR spectroscopy is in chemical analysis to determine the changes in chemical structure which may occur on exposure.

4. CONCLUSION

The variety of spectroscopic methods now available can be used to provide considerable information on radiation effects on polymeric materials. These applications are summarized in Table I. Improvements in instrumentation and data analysis procedures are continuing and the development of new spectroscopic techniques promise new insights into polymer structure and behavior.

References

[1]   Klopffer, W. Introduction to polymer spectroscopy, Springer verlag Berlin, Heidieberg, 2000. Germany.

[2]   Hummel, D. O. (ed.). Polymer Spectroscopy, Verlag Chemie; Weinheim. Germany. 2001.

[3]   Iring, K. J. (ed.). Structural Studies of Macromolecules by spectroscopic methods. Wiely, London, U.K., 2001.

[4]   Philips, E. (ed.). Polymer photo physical Champan and Hall, London. UK. 2002.

[5]   Ghiggino K. P., Philips D., Robert. A., *J. Adv. Polym, Sci,* 2002, UK.

[6]   Frank C. W., Semerk S.N., *Adv. Polymer Sci.,* 2002, U.K.

[7]   Ghiggino K. P., Bigger S. W. Smith, T. A. Sklton, P. F. and Tan, K. L. in Photo-physics of poly Hogle. C. E. and Tarkelson, J. W. (eds.). *Acs. Symp. Set.* No., 360, Am. Chem. Soc. Washington, 2001, Chapter 30-USA.

[8]   Zbinben R., Infrared Spectroscopy of High Polymers, Academic Press New York, USA. (2002).

[9]   Pointer; P. S. Coleman; M.M. Koenig J.L. The Theory of Vibrational spectroscopy and its application to polymeric materials. Willey, New York, USA. 2003.

[10]   Siester, H. W. Holland - Moritz, K. Infrared and Roman Spectroscopy of polymers. Marcel-Dekker, New York- USA. 2003.

[11]   Koenigaj L., *Adv. Poly. Sci.* 2004 (55), U.K.

[12]   Hummel, D. O. Scholl. F. Der Polymer Und Konstoffanaly Se (ed.) Verlage Chemise. Germany, 2001.

[13]   Grassie, N. Scott, G., Polymer Degrdation and Stabablization, Cambridge University Press. Cambridge UK. (2004).

[14]   Atkison, G.H. Time Resolved Vibrational press – Spectroscopy Academic Press -New York, USA (2004).

[15]   Atkin Son; g.H. Adv. Infrared and Roman Spectroscopy, New York. USA(2004).

[16]   Machauchlan, K.A. Magnatic Resonance, University Press Oxford – UK. (2004).

[17]   Ranby, B. Rabek, J. F. Esrspectro Scopy in polymer research, Spring, Berlin – Germany (2005).

[18]   Roverym F. A. High Resolution NMR of Macromolecules Academic Press, New York, USA, (2005).

[19]   Sohma; J. Sakagundry, M. *Adv. Polym Sci*. UK. (2005).

[20]   Von Meer Wall; E. D. *Adv. Polym. Sci.* UK., (2006).

[21]   Ghuggino, K.P. Chemistry in Australia (2008). Australia, 54, 450.