

IDENTIFICATION OF POLYMERS BY NMR AND IR SPECTRA

Shipra Singhal

Research Scholar, Calorx Teacher's University, Ahmedabad, Gujarat, India

ABSTRACT

Due to the growing interest in nanocomposites, a molecular characterization of these materials is essential for the understanding of their properties and for the development of new materials. Spectroscopic techniques that bring information at a molecular level are unavoidable when characterizing polymers, fillers and composites. Selected examples of the application of fluorescence, solid-state nuclear magnetic resonance (NMR), infrared and Raman spectroscopies, illustrate the potential of these techniques for the analysis of the filler surface, the evaluation of the state of filler dispersion in the host matrix, the extent of interaction between the polymer and the filler particles or the dynamics of polymer chains at the polymer–filler interface.

Keywords: nanocomposites; spectroscopy; polymer-filler interface; fluorescence; NMR; infrared; Raman

INTRODUCTION

NMR spectroscopy is a significant analytical technique that is broadly used to contemplate the structure and properties of macromolecules. The primary investigations of polymers were accounted for by Apart (1) just about a year after the disclosure of atomic reverberation in mass issue (2, 3). It was seen that normal elastic at room temperature gives a proton line width more like that of a portable fluid than of a solid, however that the reverberation expands at temperatures moving toward the glass change temperature. This was perceived as being identified with an adjustment in chain elements. NMR methods grew quickly after these underlying perceptions, both for polymers in arrangement and in the solid state.

Arrangement NMR has developed as one of the chief methods for polymer portrayal due to its high goals and affectability. It was seen in the early investigations that the substance shifts are delicate to polymer microstructure, including polymer stereochemistry, regioisomerism and the nearness of branches and imperfections.

These perceptions prompted an improved comprehension of polymer microstructure and polymerization components. With the approach of higher attractive fields and improved NMR methods and spectrometers, it has gotten conceivable to characterize even low degrees of deformities in polymer chains. The NMR spectra are touchy to the nuclear level structure and

numerous signs are seen in high resolution spectra. The correlation assignments in the early investigations were built up by contrasting the spectra with those of model mixtures. All the more as of late the improvement of spectral altering methods and multidimensional NMR has made it conceivable to dole out the spectra without falling back on model mixtures. The assignments have been built up for carbons and protons, yet additionally for any silicon, nitrogen, phosphorus or fluorine particles that might be available. The natty gritty micro structural portrayal has prompted a more profound comprehension of polymer structure-property connections.

The NMR examination of polymers in the solid state rose after the arrangement ponders since solid state NMR spectra are increasingly hard to procure and require greater gear and ability. Solid state NMR has become such a significant technique, that most current spectrometers are fit for playing out these investigations. The enthusiasm for the solid state NMR of polymers is expected to some degree to the way that most polymers are utilized in the solid state, and now and again the NMR properties can be legitimately identified with the plainly visible properties. Solid state NMR gives data about the structure and elements of polymers over a scope of length scales and time scales. Polymers have a confined versatility in solids, and the synthetic movements can be legitimately identified with the chain adaptation. Solid state NMR is additionally a proficient method to screen the reactivity of polymers, since the concoction changes offer ascent to huge spectral changes. The unwinding times in solids depend the chain elements, yet in addition on the morphology over a length size of 20-200 Å. NMR has been widely used to gauge the length size of blending in mixtures and multiphase polymers, and the area measures in semi crystalline polymers. Solid state NMR methods have been extraordinarily extended with the Introduction of multidimensional NMR (4). These investigations have prompted an atomic level comprehension of the elements customarily saw by dielectric and dynamic mechanical spectroscopy, and a superior comprehension of the connection between polymer morphology and plainly visible properties.

NMR CHARACTERIZATION OF POLYMERS

Attractive field, assigned as B_0 , at right points to B_1 . The Larmor precession recurrence or reverberation recurrence is given by $\omega = \gamma B_0$, (1) where γ is the magnetogyric proportion. The two amounts that decide the perception recurrence for NMR signals are the magnetogyric proportion γ and the attractive field quality B_0 . Table 1 show a portion of the significant atomic properties of twists that are important to polymer scientific experts. The affectability depends both on the magnetogyric proportion and the regular bounty of the NMR dynamic cores. Protons have the most elevated affectability since they have the most elevated magnetogyric proportion and characteristic plenitude. At a field quality of 11.7 T (1 Tesla=10⁴ Gauss) the NMR signals are seen at 500 MHz. Fluorine is the second most touchy cores, yet it's anything but a typical component in polymers. Most polymers of intrigue contain carbon, and Table 1 shows that the affectability is extremely low contrasted with that of protons. In any case, the

affectability of a cutting edge NMR spectrometer is to such an extent that carbon spectra can be routinely watched.

Nitrogen is likewise a typical component in polymers yet it is hard to think about on account of its low magnetogyric proportion and regular bounty. ^{15}N NMR considers are conceivable, yet simply after isotopic naming. The affectability of silicon and phosphorus is middle between that of protons and carbons, and gives a significant test of those polymers containing these components. The NMR range is typically seen by applying a radio recurrence (rf) pulse close to the reverberation recurrence and observing a free acceptance rot (FID). The NMR range, a plot of force versus recurrence, is acquired by Fourier change of the watched sign. The sign recurrence (or concoction move) is accounted for comparative with some reference compound. The incorporated sign power is relative to the quantity of cores. This property is significant in light of the fact that it enables us to utilize NMR as a quantitative instrument.

The parting of the vitality levels within the sight of the attractive field prompts a populace contrast between the upper and lower levels as controlled by the Boltzmann appropriation. At the point when the turn framework is put in no equilibrium position by Table 1. Atomic properties of enthusiasm for polymer science.

Table 1 Nuclear properties of interest in polymer science.

Isotope	Abundance (%)	Spin	Sensitivity [^]	Frequency (MHz)"
^1H	99.98	$\frac{1}{2}$		
^{19}F	100.0	$\frac{1}{2}$		
^{29}Si	4.7	$\frac{1}{2}$		
^{31}P	100.0	$\frac{1}{2}$		
^{13}C	1.1	$\frac{1}{2}$		
^2H	0.015	1		
^{15}N	0.365	$\frac{1}{2}$		

POLYMER CHAIN DYNAMICS

The chain elements are of impressive interest since they can regularly be straightforwardly identified with the mechanical properties. The movements in polymers happen over an extremely wide time scale running from picoseconds to several seconds. While no single NMR technique can gauge the elements over this range, various NMR methods can be utilized in mix to test the elements over a scope of time scales. Figure 1 condenses the range in relationship times that different unwinding estimations, lineshape estimations and trade tests are delicate to. The quickest movements can be examined with the T_1 , T_2 and NOE unwinding rate estimations. A few lineshape and unwinding methods can be utilized to test chain movement in the middle recurrence system. Solid state 2D trade trials that relate the compound moves when some trade procedure can be utilized to gauge moderate trade. As far as possible on the timescale is dictated by the T_1 unwinding time.

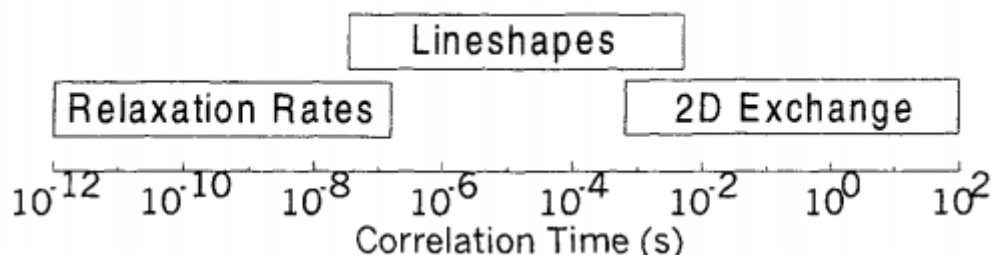


Figure 1 The time scales and methods for measuring polymer dynamics by NMR.

The chain elements of polymers in arrangement are regularly researched by means of the T_1 and T_2 unwinding times and the atomic Overhauser impact. The unwinding is brought about by fluctuating attractive fields from nuclear movement. These movements can cause unwinding just to the degree that they have a part at the thunderous recurrence.

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} G(\tau) e^{-i\omega\tau} d\tau$$

The appropriation of motional frequencies is given by the spectral densities $J(\omega)$ where $G(T)$ is the autocorrelation capacity of an intern clear vector associating the cores. To utilize this condition it is important to embrace a model for $G(T)$. The models extend structure the broadest to quite certain models fusing synthetic highlights, for example, llbratlons, tacky Tran's isomerizations and longer range segmental movements. The least difficult model is for an unbending circle Immersed in a thick continuum where the loss of memory of the past state is an exponential and is given by

$$G(\tau) = e^{-\tau/\tau_c}$$

A short estimation of TC relates to the movement of a little particle or an adaptable polymer chain, while a long worth compares to an enormous atom or a solid chain. The unwinding times give data about the chain elements since they depend in various manners on the spectral densities. The dipole-dipole commitment to the turn cross section unwinding of a carbon being loose by close by protons is given by

$$\frac{1}{T_1^{DD}} = \frac{n}{10} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2 \hbar}{r^{-6}} \{ J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C) \}$$

where n is the quantity of connected protons, μ_0 is the vacuum attractive piousness, γ_H and γ_C are the proton and carbon magnetogyric proportions, ω_H and ω_C are the proton and carbon

reverberation frequencies and r is the intern clear separation. The turn unwinding and the atomic Overhauser upgrade depend in various manners on the spectral densities. The general technique for estimating the chain elements is to quantify however many parameters as could be allowed at a few attractive field qualities and temperatures and discover a model for $G(t)$ that fits all of the data.

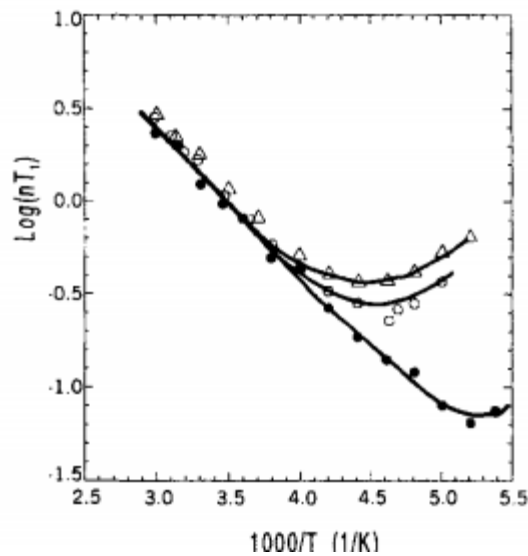


Figure 2 The dependence of the spin-lattice relaxation rate for polyisoprene on inverse temperature at (●)25, (○)90 and (△)125 MHz.

Figure 2 shows a plot of the turn cross section unwinding time for the methylene carbons of polyisoprene as an element of opposite temperature at a few frequencies. It ought to be noticed that the carbon unwinding experiences a base and is very touchy to temperature. The lines through the information were determined for a biexponential connection work. Different models additionally gave a solid match to the information as long as the models had two well-isolated connection times. The actuation vitality for the chain movement can likewise be gotten from this investigation. The enactment vitality for the methylene carbon in polyisoprene is 13.3 kJ/mol.

It is regularly hard to fit the elements of the entirety of the carbons in a polymer with similar parameters. Polymers in arrangement are very portable and the side chains may encounter movement comparative with the principle chain molecules. In such cases the side chain particles will have distinctive connection times and actuation energies than the primary chain iotas. One of the upsides of utilizing NMR to characterize chain elements is that it gives a nuclear level proportion of the chain elements.

INSTRUMENTS AND TESTING METHODS FOR POLYMER CHARACTERIZATION

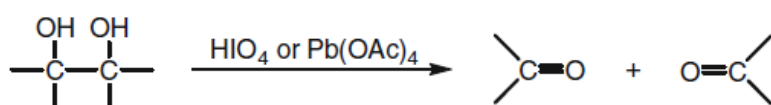
There are various instruments accessible for polymer characterization. For the substance structure characterization of polymers, infrared spectroscopy (IR), Raman spectroscopy, bright noticeable spectroscopy (UV-Vis), atomic attractive resonance spectroscopy (NMR), and electron turn reverberation spectroscopy (ESR) are regularly utilized. To think about the structure and morphology of polymers, X-beam dif-division (XRD), transmission electron microscopy (TEM), checking electron microscopy (SEM), and nuclear power microscopy (AFM) are utilized by and large. The warm properties of polymers are portrayed by differential checking calorimetric (DSC), dynamic mechanical examination (DMA), warm mechanical analyzer (TMA), and warm gravimetric investigation (TGA). The mechanical properties of polymers are considered by Instron. We will talk about the rule of each instrument quickly, and afterward show models how the polymers are being described by various instrument.

In industry, there are numerous standard testing strategies being created to portray polymers by worldwide association and various nations. The universal standard association (ISO) standard is a worldwide exertion to create standard test. In the USA, there is the American Society for Testing and Materials (ASTM) to set up the standard. The British Standards Institute (BSI) sets up British's measures. In Taiwan, the measures of testing techniques (CNS) adhere to other nations' principles. If you don't mind allude to the tests at whatever point you are out of luck. They are accessible by buying them through every standard association. You can likewise discover them in the majority of libraries and Taiwan Standard Bureau. We won't talk about them here.

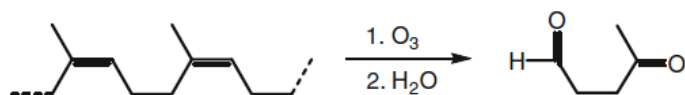
CHARACTERIZATION OF CHEMICAL STRUCTURES OF POLYMERS

Synthetic Reaction Method

To decide the synthetic structure of polymers through concoction response strategy is an ease examination however needs huge example size (1 gram). For instance, the area of straight on structure (1, 2-diol) on polyvinyl liquor can be controlled by the accompanying response.



The structures of polydienes can be resolved by means of ozonolysis. Ozonolysis of characteristic elastic, for instance, trailed by hydrolysis of the transitional ozonide under reductive conditions, yields 4-ketopentanal, which sets up the structure as the head-to-tail 1, 4-expansion polymer of 2-methyl¹, 3-butadiene (isoprene).



The measure of twofold bonds in the polymer chain can be dictated by the blanching of known measure of iodine arrangement through the expansion of response of iodine to the twofold bonds.

Infrared Spectroscopy

The infrared spectra of polymers are come about because of the diverse IR assimilation of concoction bonds (vibration progress) of endless supply of IR. The measure of vibration progress can be communicated by

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{k}{M_x M_y / (M_x + M_y)}}$$

where ν is extending recurrence in cm^{-1} , M_x , M_y the majority of two particles associated with extending, (grams), C is the speed of light, 2.998×10^{10} cm/s, and k is power steady, dynes/cm; single bond (5×10^5 dynes/cm), twofold bond (10×10^5 dynes/cm), and triple bond (15×10^5 dynes/cm). Infrared recurrence is generally communicated in units of wave number, characterized as the quantity of waves per centimeter. Common instruments filter the scope of around $700\text{--}5,000 \text{ cm}^{-1}$. This recurrence go relates to energies of around $2\text{--}12$ kcal/mol. This measure of vitality is adequate to influence bond vibrations (movements, for example, bond extending or bond twisting) yet is considerably not exactly would be expected to break bonds. These movements are represented in Fig.3

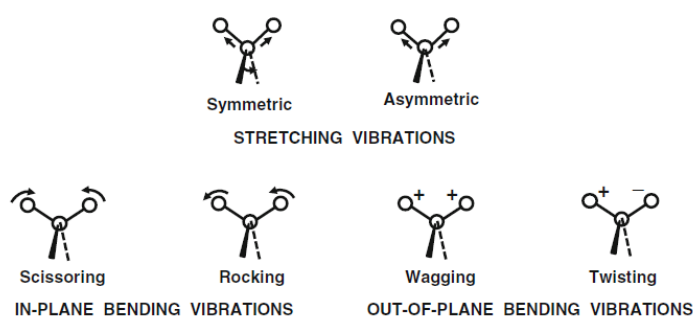


Fig. 3 Vibrations of a group of atoms (+ and – signify vibrations perpendicular to the plane of the paper)

Specific kinds of obligations of natural particle normally stretch inside certain somewhat thin recurrence ranges which are extremely valuable to decide the synthetic structure of atom. Table 2 gives the scopes of extending frequencies for certain bonds usually found in natural particles.

The compound structures of obscure polymers can be perceived for the most part through their particular IR assimilation recurrence. In any case, their careful substance structures can't reason from IR spectra just, except if they can be contrasted and known information or from the IR spectra of their monomers. Figure 4 shows the distinction of IR spectra among polyimide and its synthetic rehashing unit model compound is at the p-substituting linkage between the sweet-smelling structures of monomers with C–H twisting at $650\text{--}900\text{cm}^{-1}$.

Table 2 Infrared stretching frequencies of some typical bonds

Bond type	Class compound	Frequency range (cm^{-1})	
Single bonds to hydrogen	alkanes	2,850–3,000	
	alkenes and aromatic	3,030–3,140	
	alkynes	3,300	
	alcohols and phenols	3,500–3,700 (free)	
		3,200–3,500 (hydrogen-bonded)	
	carboxylic acids	2,500–3,000	
	amines	3,200–3,600	
	thiols	2,550–2,600	
	Double bonds	alkenes	1,600–1,680
		imines, oximes	1,500–1,650
aldehydes, ketones, esters, acids		1,650–1,780	
Triple bonds	alkynes	2,100–2,260	
	nitriles	2,200–2,400	
Substitute aromatics	ortho	750	
	para	830	
Halide	C–F	2,962–2,853	
	C–Cl	800–600	
	C–Br	600–500	

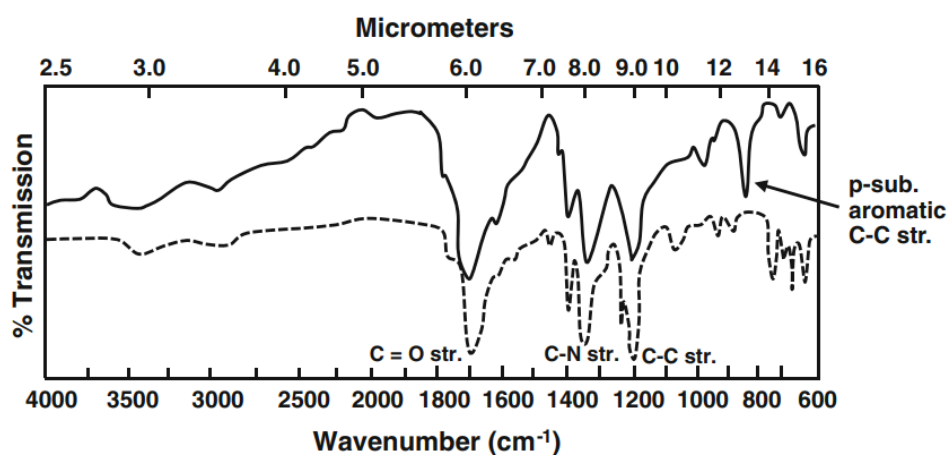


Fig. 4 Infrared spectrum (KBr pellets) of polyimide (—) and model compound

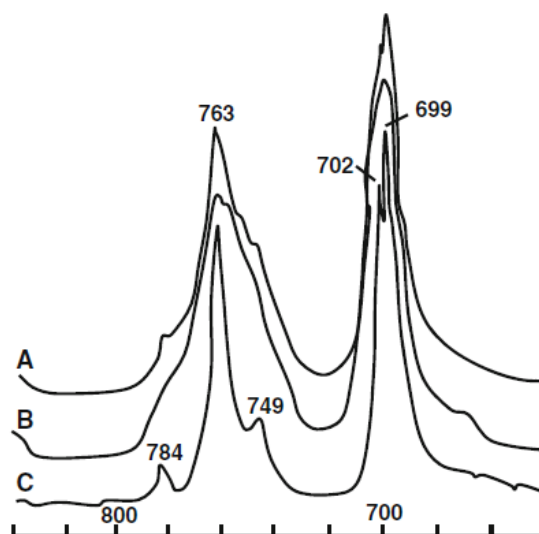


Fig. 5 Fourier transform infrared spectra of isotactic polystyrene in the $640\text{--}840\text{ cm}^{-1}$ region:(A) semicrystalline; (B) amorphous; and (C) the difference spectrum obtained by subtracting B from A

The IR of isotactic polystyrene can be gotten by subtracting the spectrum of shapeless polystyrene from the spectrum of semi crystalline polystyrene as appeared in Fig. 5. A well-characterized sharp retention is uncovered which demonstrates the benzene rings are "solidified" into moderately explicit adaptations in the crystalline state.

Raman Spectroscopy

Like IR spectroscopy, Raman gets from vibrational changes in atoms. At the point when unmistakable light encroaches on atoms, the light is dispersed. The recurrence of the dissipated light fluctuates as indicated by the vibrational methods of the dispersing atoms. This alluded to as the Raman impact. While IR ingestion spectra are demonstrative of unsymmetric bond extending and twisting, the Raman impact reacts to the symmetric vibrational modes.

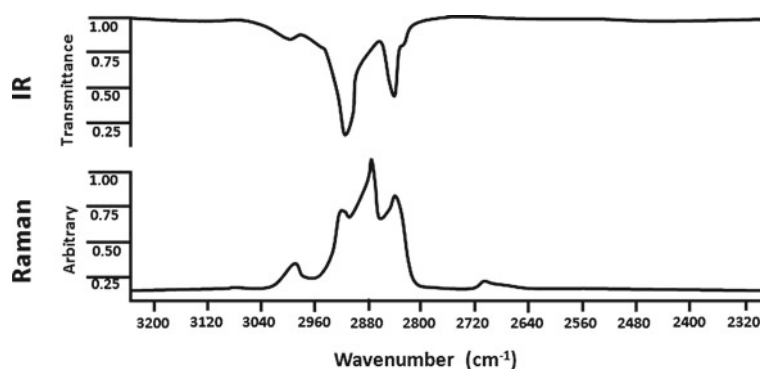


Fig. 6 Comparison between IR and Raman of trans-poly pentamer

Polar gatherings of a particle give the most extreme IR signals though nonpolar ones offer

ascent to most exceptional Raman signals. Along these lines IR and Raman spectroscopy are corresponding. Matched IR and Raman spectra of a similar compound have a synergistic impact in advancing under-remaining of basic data.

Raman is generally receptive to balanced extending in C–C bonds. It is helpful to think about the conformational structure of polymer chains by contrasting spectra and those of long-chain "model" alkanes. The stereoisomers of polymer is gotten by pivot around single bonds, so the Raman can be utilized to contemplate the cis-trans isomerism in elastomers, sulfur crosslinks in elastic, and polymer disfigurements. Since Raman dissipating by water is insignificant contrasted and water's extraordinary IR assimilation, Raman is especially valuable in conformational investigations of biopolymers in watery arrangement. Figure 6 shows the correlation among IR and Raman of trans-poly pentenamer. The Raman shows more component than that of IR because of the even structure of alkane ($-C-C-$ at $2,900\text{ cm}^{-1}$) and alkene ($-C=C-$ at $3,000\text{ cm}^{-1}$). The examination of IR and Raman spectrum of poly(3-hexyl thiophene) (P3HT). The balanced C–C extending is overwhelmed in the Raman spectrum while the C–H extending is commanded in the IR spectrum. The P3HT is integrated by Grignard metathesis response as appeared in Fig. 8.

The yield can be higher than 70 %. The guideline of metathesis combination will be talked about in Sect. 9.4.

UV-Visible Spectroscopy

Bright noticeable (UV–Vis) spectroscopy is utilized to distinguish the chromospheres of issue subjectively and quantitatively when the issue experiences n pm and p pm progress upon light illumination. Due to its affectability ($\sim 10^{-5}$ molar), UV–Vis spectroscopy has been especially valuable in recognizing the pollutions in polymers, for example, leftover monomer, inhibitors, cell reinforcement, etc.

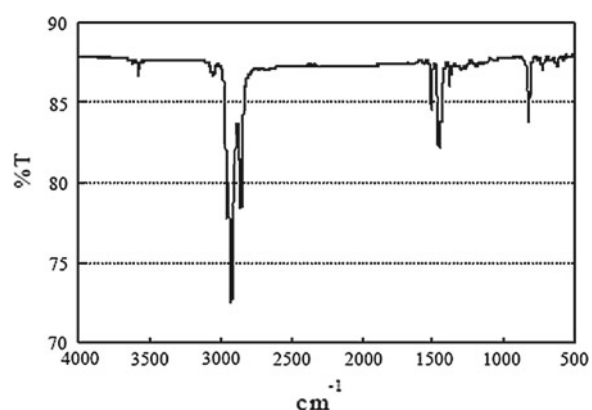


Fig. 7 IR spectrum (top) and Raman spectrum (bottom) of P3HT

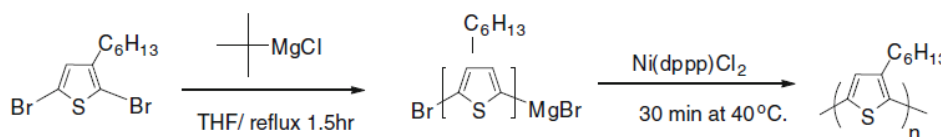
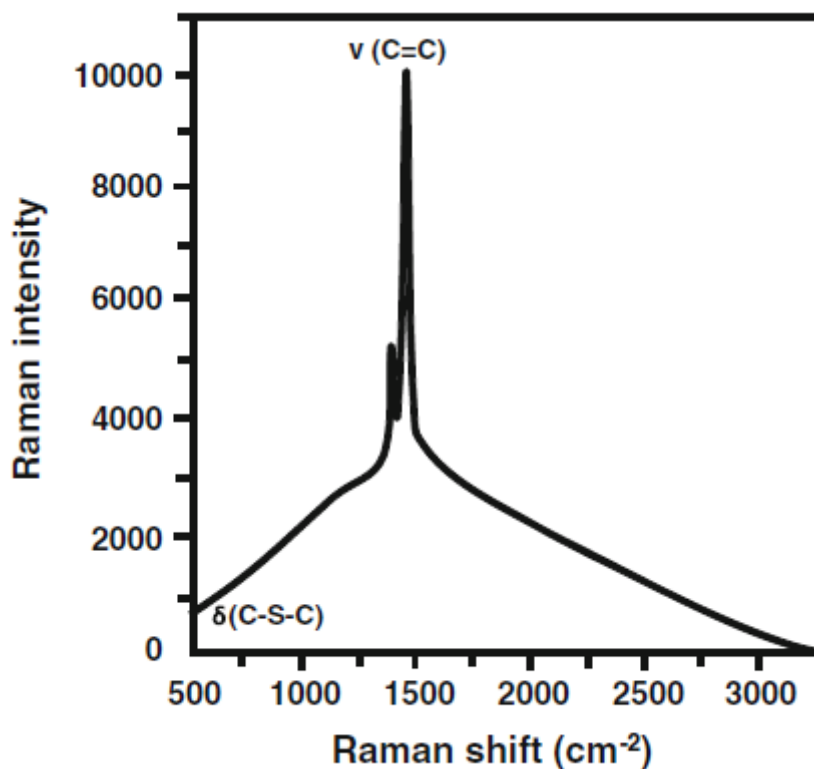


Fig. 8 Synthesis of P3HT using Grignard metathesis reaction

Styrene monomer in polystyrene, for instance, might be resolved quantitatively utilizing styrene's k_{\max} at 292 nm. After the styrene is polymerized, the 292 nm pinnacle of styrene vanishes and shows the k_{\max} at 203 and 254 nm of benzene for polymer. Figure 9 shows a run of the mill bright assimilation spectrum of natural compound. Not at all like infrared spectra, UV-Vis spectra are very wide and by and large show just few pinnacles. The pinnacles are accounted for as the wavelengths where maxima happen. The conjugated, unsaturated Ketone whose spectrum is appeared in Fig. 5.7 has an extraordinary retention at $k_{\max} = 232$ nm and an a lot flimsier assimilation at $k_{\max} = 330$ nm. The band at shorter wavelength relates to a p

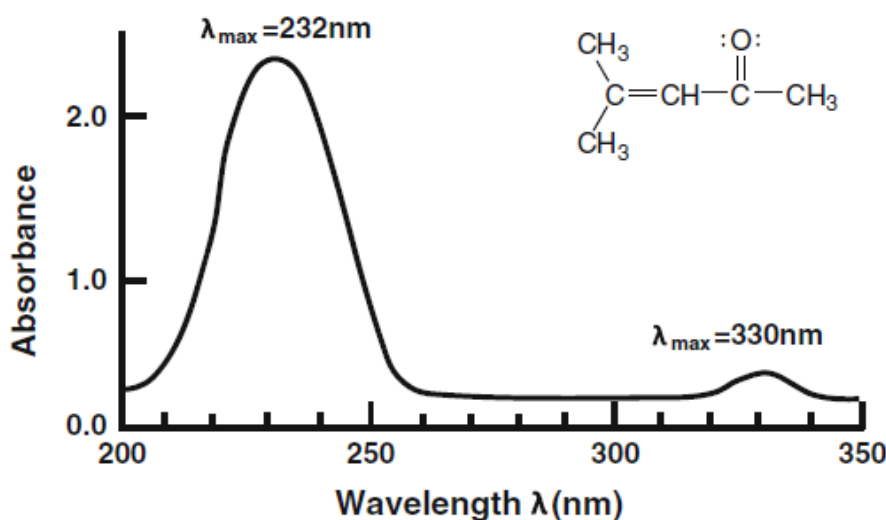


Fig. 9 The absorption spectrum of 4-methyl-3- penten-2-one

Electron progress, though the more extended wavelength, flimsier force band corresponds to a change of the nonbonding electrons on the carbonyl oxygen iota. The force of a retention band can be communicated quantitatively. Band power relies upon the specific atomic structure and furthermore on the quantity of engrossing particles in the light way. Absorbance, which is the log of the proportion of light forces entering and leaving the example, is given by Beer's law as beneath where s is the molar absorptive (now and then called the eradication coefficient), c is the convergence of the arrangement in moles per liter, and l is the length in centimeters of the example through which the light passes.

$$A = \epsilon cl$$

The worth s for any top in the spectrum of a compound is a steady trait of that specific atomic structure. For instance, the estimations of s for the tops in the spectrum of the unsaturated Ketone appeared in Fig. 9 are $k_{\max} = 232 \text{ nm}$ ($s = 12,600$) and $k_{\max} = 330 \text{ nm}$ ($s = 78$). UV-Vis spectra are most generally used to distinguish conjugation. When all is said in done, atoms with no twofold bonds or with just one twofold bond don't ingest in the locale of UV to unmistakable (200–800 nm). Conjugated frameworks do retain there, in any case, and the more noteworthy the conjugation, the more extended the wavelength of greatest ingestion, as found. Thusly, the greater part of the conjugated polymers display retention in the unmistakable range.

CONCLUSION

The importance of various spectroscopic techniques for investigating polymer composites were discussed in this review. While fluorescence spectroscopy, contrary to infrared and Raman spectroscopy, cannot provide detailed information on molecular structures, the fluorescence resonance energy transfer between two chromophores is an important phenomenon for the

analysis of polymer–filler interfaces. The fluorescence behavior of small molecules can be used to probe confinement effects in filled systems or intercalation and exfoliation in clay nanocomposites. Solid-state NMR can identify the silanol hydroxyl groups present on the silica surface and analyze their interactions with the polymer chains. Moreover, solid-state NMR is probably one of the most effective tool for the analysis, through the determination of the relaxation times, of the dynamics of polymer chains at the interfacial region of filled systems. Over the years, infrared spectroscopy has been extensively used to characterize a wide range of materials through bands associated with the functional groups of the fillers or the polymers. Near-infrared spectroscopy, which probes overtones and combination bands, can be used to analyze the chemical groups that display strong absorptions in the mid-infrared. It is particularly interesting for the determination of chain orientation in the case of thick samples analyzed in transmission. Raman spectroscopy has become a key technique for the characterization of carbon-based materials that display, due to resonance-enhanced scattering effects, strong, well-defined bands even if used at very small amounts in the composite. Combined with scanning probe microscopy, Raman spectroscopy has been launched to a new dimension with unprecedented insights into phenomena relevant to the field of nanomaterials. Nevertheless, it should be recalled that the laser power must be controlled in order to avoid sample heating that can shift the Raman bands. In this study, N-vinylcaprolactam was polymerized in solid state by radiation. Polymerization was carried out in vacuum and in open atmosphere at room temperature. The following conclusion were derived from this study: 1. The rate of polymerization was higher in open air and limiting conversion was 100% in vacuum; 90% in open atmosphere. 2. Polymer obtain was gel type soluble in water and most common organic solvents. 3. FT-IR and NMR results show that polymerization proceeded by opening of vinyl group. 4. The light scattering, GPC and viscosity methods useful for molecular weight determination showed that the polymer conformation in solution highly dependent on molecular weight. Therefore, a simple relation between intrinsic viscosity and molecular weight could not be obtained. 5. X-Ray structure determination showed that the crystal structure of monomer retained its identity up to about 86% conversion. The polymer was amorphous but showed some polymer chain regularity and chain orientation up to a certain extend. 6. Mass spectrum analysis of monomer and polymer gave the fragments compatible with a vinyl group backbone chain and lactam as side group.

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