CHARACTERIZATION OF POLYMERIC SOLUTIONS: A BRIEF OVERVIEW

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Abstract. Polymers are perhaps the most important materials for the present era of science and technology. They are employed in nearly every device, involving the interior of every automobile to several biomedical applications. Their diverse properties and wide range applicability prove them to be classified as modern materials or advance materials. In context to their great potential and widespread applicability, the characterization of polymeric solution is rapid growing area for the researchers and scientists. Various techniques have been employed up till now to elucidate their various structural aspects and hidden secrets of their functional aspects. A brief review of the techniques used to characterize polymeric solutions has been presented.

1. INTRODUCTION:

Polymer molecules consist of the same repeating units, called monomers, or of different but resembling units. In the solid state, polymer molecules pack the space with little voids either in a regular array (crystalline) or at random (amorphous). The molecules are in close contact with other polymer molecules. In solutions, in contrast, each polymer molecule is surrounded by solvent molecules. The number of molecules makes many of the properties common to all polymer molecules but not shared by small molecules. A difference in the chemical structure of the repeating unit plays a secondary role [1,2].

The methodologies to investigate the structure and dynamics of polymeric systems have not grown at the same rate as the numbers of reports of novel developments. In addition, further progress in the modeling of the relations between molecular, nanoscopic and macroscopic structures and properties is needed in order to understand and predict the limits of performance that can be attained by polymers, particularly those of commercial interest.

The polymer industry is one of major importance worldwide. The 21st century can be called as the “Age of Polymers” [3].

2. POLYMER SOLUTIONS CHARACTERIZATION

The characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties.

3. PROPERTIES OF POLYMERIC SOLUTIONS - CHARACTERIZATION TECHNIQUES

A variety of lab techniques are used to determine the properties of polymers. Techniques such as wide angle X-ray scattering & small angle X-ray scattering, and small angle neutron scattering are used to determine the crystalline structure of polymers. Gel
permeation chromatography is used to determine the average molecular weight and polydispersity. FTIR, Raman, and NMR can be used to determine composition. Thermal properties such as the glass transition temperature and melting point can be determined by differential scanning calorimetry and dynamic mechanical analysis. Pyrolysis followed by analysis of the fragments is another technique for determining the possible structure of the polymer. Thermogravimetry is a useful technique to evaluate the thermal stability of the polymer. Detailed analyses of TG curves also allow us to know a bit of the phase segregation in polymers. Rheological properties are also commonly used to help determine molecular architecture (molecular weight, molecular weight distribution and branching) as well as to understand how the polymer will process, through measurements of the polymer in the melt phase [4,5].

4. CLASSICAL MEASUREMENTS IN POLYMER SOLUTIONS

4.1. Laser light scattering

Light scattering has been widely used to characterize polymer chains in a solution. It is possible to determine the weight-average molecular weight ($M_w$), the radius of gyration ($R_g$), and the second virial coefficient ($A_2$). The shape of the polymer molecule—whether it is spherical, random-coiled, or rodlike—could also be investigated. Recent technical developments have strongly enhanced the possible applications of this technique, overcoming previous limitations like sample turbidity or insufficient experimental time scales.

4.1.1. Light scattering techniques—classification

Two different light scattering methodologies can be used to elucidate the structure of polymer solutions: “Classical light scattering” (also known as “static” or “Rayleigh” scattering or MALS) which provides a direct measure of molecular mass. It is therefore, very useful for determining whether the native state of a polymer is a monomer or a higher oligomer, and for measuring the masses of aggregates or other non-native species. It also can be used for measuring the stoichiometry of complexes between different polymers.

“Dynamic light scattering”, is also known as “photon correlation spectroscopy” (PCS) or “quasi-elastic light scattering” (QELS). It uses the scattered light to measure the rate of diffusion of the polymer particles. This motion data is conventionally processed to derive a size distribution for the sample, where the size is given by the “Stokes radius” or “hydrodynamic radius” of the polymer particle. This hydrodynamic size depends on both mass and shape (conformation). Dynamic scattering is particularly good at sensing the presence of very small amounts of aggregated polymers and studying samples containing a very large range of masses. It can be quite valuable for comparing stability of different formulations, including real-time monitoring of changes at elevated temperatures [6].

4.1.2. Characterization of polymer solutions by laser light scattering technique

a) Determination of reversible association of polymeric molecules

A method for rapid detection and characterization of reversible associations of macromolecules in solution had been suggested. In these experiments, one simultaneously measures concentration and total solute scattering, a property that depends upon the product of solute mass and refractive increment of each solute species and upon the interactions, both attractive and repulsive, between solute molecules. The use of light scattering experiments provided the information about reversible associations that was comparable in scope and resolution to that currently obtainable from sedimentation equilibrium had been suggested. Since the methodology introduced, in contrast to that of sedimentation equilibrium, permitted extremely rapid acquisition and analysis of composition-dependent data, it may in principle be used to characterize reversible associations evolving with time and at equilibrium and, with the addition of sample handling robotics, may be utilized in moderately high-throughput assays for reversible macromolecular association in solutions [7].

A comparative study of the association of cyclic- and linear polymeric chains with varying chain lengths and end groups in dilute aqueous solutions had been done by laser light scattering (LLS) and stopped-flow temperature-jump measurements. Results have revealed that the heating leads to a microphase transition.

The resultant structures of inter-chain aggregates have found to be dependent on the heating rate and the chain topologies [16]. Static light scattering studies of polyelectrolyte solution indicated that the first generation complex had a coil-like conformation. The second and third generation complexes exhibit poly-
Table 1. Recent developments in the characterization of polymer solution by laser light scattering technique.

<table>
<thead>
<tr>
<th>Polymer solutions</th>
<th>Property being investigated</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macromolecule (Albumin etc.) in solution.</td>
<td>Rapid detection and characterization of reversible associations</td>
<td>Extremely rapid acquisition and analysis of composition-dependent data</td>
<td>[7]</td>
</tr>
<tr>
<td>Fluorinated alkyl methacrylate, poly(1,1,2,2-tetrahydroperfluoroctylmethacrylate) (PFOMA)</td>
<td>Solution properties</td>
<td>Hydrodynamic radius expansion factor Rh and the normalized second virial coefficient were discovered to be functions of the same interaction parameter</td>
<td>[8]</td>
</tr>
<tr>
<td>Hexanoyl chitosan and its derivatives</td>
<td>Solution properties</td>
<td>Same degree of polymer–solvent interactions had been observed</td>
<td>[9]</td>
</tr>
<tr>
<td>Carboxymethylcellulose in water</td>
<td>Polymer–surfactant interaction</td>
<td>Polymer chain shrinkage due to noncooperative binding had been observed</td>
<td>[10]</td>
</tr>
<tr>
<td>Polyacrylamide (AAm)-based hydrogels Polystyrene</td>
<td>Network microstructures Viscoelastic properties</td>
<td>Steric effect of the bulky side groups was evident.</td>
<td>[12]</td>
</tr>
<tr>
<td>Solutions of homopolymers and diblock copolymers Poly(N-isopropylacrylamide) (c-PNIPAM) and (c-PNIPAM) chains</td>
<td>Molecular interactions</td>
<td>Time dependence of fluctuations near the critical point of phase separation had been determined.</td>
<td>[15]</td>
</tr>
<tr>
<td>Polyelectrolyte solutions Precursor polymer solutions customarily used to fabricate polymer-based light-emitting diodes.</td>
<td>Association behavior of polymer chains</td>
<td>Mode of instrument being used was found to be the representative of the motion of the solvent molecules in the solution.</td>
<td>[13]</td>
</tr>
<tr>
<td>Polymers, polyethylene oxide and hydroxyethyl cellulose. Polycrylamide</td>
<td>Structural studies</td>
<td>Heating leads to a microphase transition which were observed to be dependent on heating rate and chain topologies.</td>
<td>[16]</td>
</tr>
<tr>
<td>Concentrated protein solutions.</td>
<td>Aggregate formation behavior</td>
<td>The flowerlike coil conformation had been suggested.</td>
<td>[17]</td>
</tr>
<tr>
<td>Modified Polycrylamide</td>
<td>Mesh size and homogeneity of polymer network</td>
<td>Compromising the bulk and the local solution aggregation states is essential in producing tunable and high-performance PLEDs.</td>
<td>[18]</td>
</tr>
<tr>
<td>PA/PVA interpolymer complexes</td>
<td>Structure and dynamics Viscosity</td>
<td>Polymer network with a homogenous mesh size was suggested to be the best sieving medium for separation of the proteins.</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>Molecular weight, second virial coefficient and radius of gyration</td>
<td>The characteristic network parameters were obtained.</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>Characterization of interpolymer complexation</td>
<td>The DLS method described here has the potential to be used in many aspects of protein characterization.</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>The non-hydrolyzed polymer was discovered to be more sensitive to salt than hydrolyzed polymers.</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>These complexes could be suitable as potential carrier for biomedical applications.</td>
<td>[21]</td>
</tr>
<tr>
<td>SBP/P(iPA-co-SSS) complexation</td>
<td>Complex formation between soybean peroxidase and poly(N-isopropylacrylamide-co-sodium styrene sulfonate)</td>
<td>Both the electrostatic and hydrophobic interactions play an important role in the SBP/P(iPA-co-SSS) complex formation.</td>
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<td>--------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Different types of homopolymers in low viscosity ionic liquids (ILs)</td>
<td>Solubility and chain conformation</td>
<td>The mutual interactions determined the solubility and conformation of polymers in ILs.</td>
<td></td>
</tr>
</tbody>
</table>
Characterization of polymeric solutions: a brief overview

Electrolyte behavior. All these observations could be explained by the flowerlike coil conformation, which was formed by the intra-molecular association [17].

b) Determination of interactions in polymeric solutions

An advancement in determining the interactions in polymeric solutions occurs as it had been demonstrated that the hydrodynamic radius expansion factor $Rh$ and the normalized second virial coefficient are also functions of the same interaction parameter $z$ and are proportional to the reduced solvent density at constant temperature. These results provided an important explanation of the observation that the solvent quality can be tuned by not only the solvent temperature but also the solvent density in a universal way [8]. It had been also reported that insight of conformational changes and intermolecular interactions within polymeric solutions could be determined by laser light scattering [9]. In related studies, interaction of cationic surfactants in aqueous media had been investigated by dynamic light scattering. Growth of the mixed aggregates in relation with the phase separation was elucidated in detail [10]. Dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) were also employed to determine the aggregate formation and type of chain packing in the semidilute regime of polymer, respectively [11].

c) Structure elucidation

The network microstructure and formation of hydrogels within polymeric solutions by the use of laser light scattering techniques had been being reported [12]. The fine structure of the solutions of homopolymers, diblock copolymers [13] and polymeric hydrogel solutions [14] had been illustrated by distribution of relaxation times obtained from dynamic light scattering. The chain confirmation of certain homo-polymers in ionic liquids have been elucidated by using laser light scattering and it was suggested that the mutual interactions among molecules of polymer and ILS are responsible for their extent of solubility and chain confirmations [23].

d) Determination of viscoelastic properties of the polymers

The time dependence of fluctuations near the critical point of phase separation in solutions of polystyrene in cyclohexane with high polymer molecular weights was being determined by dynamic light scattering. From an analysis of the time dependence of the experimental dynamic correlation functions in terms of a theory of coupling of dynamic modes, viscoelastic properties of the polymers in the solution could be determined [15].

e) Determination of aggregate formation

Dynamic light scattering measurements disclosed the ubiquity of large aggregate species in the precursor polymer solutions customarily used to fabricate polymer-based light-emitting diodes [18]. The mesh size and homogeneity of polymer network was evaluated by dynamic light scattering. It had been proposed that a polymer network with a homogenous mesh size of less than 10 nm was the best sieving medium for separation of the proteins [19]. A new method to measure the viscosity of concentrated protein solutions in a high-throughput format by means of dynamic light scattering had been proposed [20].

f) Complex formation

Laser light scattering has also used as a tool to confirm the complex formation between different polymer complexes [21,22]. Different interactions within these complexes have been found to be responsible for the complex formation and their further applications.

5. RHEOLOGY

Rheology is the study of the flow of matter: primarily in the liquid state, but also as ‘soft solids’ or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. The flow of these substances cannot be characterized by a single value of viscosity (at a fixed temperature). While the viscosity of liquids normally varies with temperature, it is variations with other factors which are studied in rheology.

5.1. Non-newtonian fluid mechanics

Since Sir Isaac Newton originated the concept of viscosity, the study of variable viscosity of liquids is also often called non-newtonian fluid mechanics. Theoretical aspects of rheology are the relation of the flow/deformation behavior of material and its internal structure (e.g., the orientation and elongation of polymer molecules), and the flow/deformation behavior of materials that cannot be described by classical fluid mechanics or elasticity [24,25].

5.2. Rheology of polymeric solutions

a) Determination of viscoelastic properties

The viscoelastic properties of polymers are determined by the effects of the many variables, including temperature, pressure, and time. Other important variables include chemical composition, molecular weight and weight distribution, degree of branching and crystallinity, types of functionality,
<table>
<thead>
<tr>
<th>Polymer solutions</th>
<th>Property being observed</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wormlike micellar system.</td>
<td>Mechanical and optical measurements.</td>
<td>Steady-state and transient behavior of the mean rheological and optical quantities.</td>
<td>[29]</td>
</tr>
<tr>
<td>HECs and hmHECs solutions.</td>
<td>Rheo-optical analysis</td>
<td>The occurrence of aggregates was evident with transition from intra- to intermolecular polymer micelles in shear flow.</td>
<td>[30]</td>
</tr>
<tr>
<td>Isolated high molecular weight (MH) polymer chains.</td>
<td>Mechanical properties</td>
<td>The results obtained were found to be roughly in accord with Zimm theory.</td>
<td>[31]</td>
</tr>
<tr>
<td>Film forming polymeric solutions.</td>
<td>Mechanical properties</td>
<td>The investigated methods were unable to characterize the properties of the thin films on living skin satisfactorily.</td>
<td>[32]</td>
</tr>
<tr>
<td>Polystyrene nanoparticles.</td>
<td>Shear flow</td>
<td>Conformational changes in gelatin can be driven by local fluid mechanics.</td>
<td>[33]</td>
</tr>
<tr>
<td>Polyacrylamide solution.</td>
<td>Elongational flow</td>
<td>The strain rate in the flow direction had been determined.</td>
<td>[34]</td>
</tr>
<tr>
<td>Poly(vinyl methyl ether) homopolymer melt.</td>
<td>Normal stresses measurement.</td>
<td>Improved rheo-optical instrument had been suggested.</td>
<td>[36]</td>
</tr>
<tr>
<td>Solutions of polystyrene in diethyl phthalate.</td>
<td>Thinning and breakup of filaments.</td>
<td>Strong extension thinning had been observed after certain concentration.</td>
<td>[37]</td>
</tr>
<tr>
<td>Polyarylsulfone polymers in both N, N, dimethylacetamide (DMAc) and ionic liquid 1 butyl-3-methylimidazolium chloride ([Bmim] Cl) cellulose/1-butyl-3-methylimidazolium chloride</td>
<td>Rheological behavior</td>
<td>DMAc, as concentration increases viscosity increases, while the rheological behavior of the PASF/(Bmim) Cl solution exhibits a maximum in the viscosity-concentration plots.</td>
<td>[39]</td>
</tr>
<tr>
<td>Poly(acrylonitrile-co-itaconic acid) (poly(AN-co-IA)) in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) acrylic copolymers in 1-butyl-3-methylimidazoliumchloride ([Bmim]Cl)</td>
<td>Rheological behavior</td>
<td>The existence of microheterogeneity in the solution system.</td>
<td>[40]</td>
</tr>
<tr>
<td>Poly(AN-co-IA)/[BMIM]Cl solutions are typical neutral polymeric liquids for the concentrated solutions but have shown a more complicated behavior at high deformation rates.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>salvation capacity of [BMIM]Cl for poly(AN-co-AM) can be evidently improved due to the extrahydrogen bond interactions between NH2 group ofAMand anion of [BMIM]Cl.</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
component concentration, dilution with solvents or plasticizers, and mixture with other materials to form composite systems. Viscoelastic behavior reflects the combined viscous and elastic responses, under mechanical stress of materials which are intermediate between liquids and solids in character [26].

b) Structure elucidation

Investigations of the rheological properties of associative polymer solutions had been reviewed recently [27]. These studies could easily illustrate various structural aspects of these macromolecular structures. Rheology provides a unique opportunity; to relate the microstructure of polymer molecules to their macroscopic properties [28], to explain the shear flow behavior of a classical viscoelastic wormlike micellar system [29], to determine the strain rate [34,36] and in order to investigate the occurrence of aggregates [30].

The dynamics of isolated high molecular weight polymer chains dissolved in a nonentangled semidilute solution of a low molecular weight polymer by using a probe molecule have been reported in literature, although the results obtained were found to be roughly in accord with Zimm theory [31]. Film forming polymeric solutions as a novel approach for skin drug delivery were developed and characterized concerning their mechanical properties and water vapor permeability. Their mechanical properties determined in vitro were found to be not predictive for the flexibility and abrasion resistance observed on living skin [32].

Flow can change the rate at which solutes adsorb on surfaces by changing mass transfer to the surface, but moreover, flow can induce changes in the conformation of macromolecules in solution by providing sufficient stresses to perturb the segmental distribution function. However, there are few studies where the effect of flow on macromolecules had been shown to alter the structure of macromolecules adsorbed on surfaces. A study had been made regarding that how the local energy dissipation alters the adsorption of gelatin onto polystyrene nanoparticles [33]. A novel optical cross-slot channel rheometer had been described generating two-dimensional and isothermal complex flows of polymer melts.

This was made possible by lubricating the channel front and back viewing windows. Flow-induced birefringence and particle tracking velocimetry were reviewed and used to investigate the cross-slot flow of a low density polyethylene melt involving mixed shear and planar extensional deformations. This new device was suggested to solve the issue of end effects in flow birefringence experiments where no variations of the optical properties along the light path were expected. It was found to greatly facilitate the interpretation of stress field data by providing reliable measurements of the polymer melt extinction angle and retardation, with a spatial resolution of one tenth of a millimeter. At the same time, it offered an enhanced temperature control and an increased optical accuracy due to an improved laser beam shaping [35].

The thinning and breakup of filaments of semidilute solutions of polymer could be investigated with a capillary breakup extensional rheometer. The onset of the elastocapillary balance was molecular weight dependent and the coil stretch transition of the polymer is shifted close to the breaking point and to small filament diameters [37]. The rheological behavior of various polymers in different ionic liquids has been studied by our group and a detailed account about the interactions of these solutions and their effect on their rheological studies is being elaborated in detail [38-41].

6. VISCOSITY

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. Viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity, an idea about molecular weight could be obtained. Viscosity techniques are very popular because they are experimentally simple. They are, however less accurate; the determined molecular weight and the viscosity average molecular weight is less precise. For example, \( M_w \) depends on a parameter which depends on the solvent used to measure the viscosity. Therefore the measured molecular weight depends on the solvent being used. Despite these drawbacks, viscosity techniques are very valuable.

6.1. Polymeric solutions—viscosity measurements

The reduced viscosities of an ultrahigh molar mass polyethylene oxide sample in aqueous solution were measured both by an ordinary glass viscometer and by a viscometer constructed with a polytetrafluoroethylene capillary. After correction for solute adsorption and slippage, respectively, the two sets of data coincide well and gave a common linear reduced viscosity plot down to extremely dilute concentration regime [43]. In another studies, it has
Table 3. Recent developments in viscosity measurements of polymer solutions.

<table>
<thead>
<tr>
<th>Polymer solutions</th>
<th>Instruments being used</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene, linear and branched polyvinyl acetate solutions</td>
<td>Ordinary glass viscometer and by a viscometer constructed with a polytetrafluoroethylene capillary.</td>
<td>Common linear reduced viscosity plot down to extremely dilute concentration regime has been obtained.</td>
<td>[43]</td>
</tr>
<tr>
<td>Poly (vinyl alcohol) (PVA) and its derivatives.</td>
<td>Ubbelohde viscometer</td>
<td>Anomalous viscosity behavior of neutral polymer solutions at low concentrations was due to the improper technique by which the viscosity of polymer solution was determined.</td>
<td>[44]</td>
</tr>
<tr>
<td>Dextran samples and amphiphilic dextran derivatives</td>
<td>Ostwald-type capillary viscometer</td>
<td>The interdependence between Fedors parameter and other viscometric characteristics (intrinsic viscosity, Huggins coefficient) was evidenced.</td>
<td>[45]</td>
</tr>
<tr>
<td>Aqueous solutions of polyethylene oxide (PEO)</td>
<td>Opposing jet elongational rheometer</td>
<td>The elongational viscosities of these solutions were greatly enhanced by interactions between the polymer chain and surfactant micelles.</td>
<td>[46]</td>
</tr>
<tr>
<td>Solutions of poly(methyl methacrylate) (PMMA).</td>
<td>Falling cylinder type viscometer.</td>
<td>Viscosity along with the phase state and the density of the solutions had been determined.</td>
<td>[47]</td>
</tr>
<tr>
<td>Poly(ethylene oxide) in aqueous solutions of hydrogen chloride</td>
<td>Jacketed Ubbelohde viscometer.</td>
<td>Intrinsic viscosity was measured to investigate effect of temperature and concentration of H3O+ ions.</td>
<td>[49]</td>
</tr>
<tr>
<td>Polymer solutions from heavy oil reservoirs.</td>
<td>Brookfield DV-II+ Viscometer</td>
<td>The minimum and optimum effective viscosities of polymer solution increased with increasing oil viscosity.</td>
<td>[50]</td>
</tr>
<tr>
<td>Dilute solutions of flexible polymers</td>
<td>New coquette-type Viscometer</td>
<td>Direct determination of the intrinsic viscosity was investigated.</td>
<td>[51]</td>
</tr>
<tr>
<td>Sulfonated Polyacrylamide Polymers</td>
<td>Rotary rheometer</td>
<td>The viscosity and retention of copolymers had been studied under aerobic conditions with and without the sacrificial agent.</td>
<td>[52]</td>
</tr>
<tr>
<td>Polyelectrolytes</td>
<td>Rheometer</td>
<td>The viscosity increase agrees with viscosity scaling theory for polyelectrolytes in the entangled regime.</td>
<td>[53]</td>
</tr>
</tbody>
</table>
been suggested that the effective diameter of the viscometer capillary and the surface property of the capillary wall were found to be important factors in determining the accuracy of method being used [44]. Various polymers have been studied by viscometric measurements in order to determine intrinsic viscosity, Huggins coefficient [45,48,49], elongational viscosities [46], high-pressure viscosity and density of solutions [47].

The minimum and optimum effective viscosities of polymer solution of high oil reservoirs was also investigated by these measurements [50] and it was found that the resulting viscosities is in direct relation to the viscosity of oil. Later, a new Couettetype viscosimeter with a magnetically suspended rotor allowed to directly determine the intrinsic viscosity [51]. The viscosity and retention of several copolymers had been studied under aerobic condition with and without the sacrificial agent. The viscosity at high temperature had been studied as a function of aging time, shear rate, sulfonation degree and molecular weight. By increasing temperature, less relative reduction in polymer solution viscosity was observed for the polymer with lower molecular weight [52].

In another investigation, the viscosity of several polyelectrolytes was measured in both salt free solutions and solutions in the high salt limit. The increase in viscosity in monovalent salt solution appeared to be heavily influenced by the molecular characteristics of the polymers such as monomer weight, molecular structure, and chain conformation [53].

7. X-RAY DIFFRACTION STUDIES
X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

Applications of XRD
X-ray diffraction (XRD) has long been successfully used to study various aspects of these structures in semicrystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers [54-63].

While many of the well-established methods for the determination of molecular structure, evaluation of crystallinity and analysis of texture, continue to be improved to enhance the speed and precision of these measurements.

7.1. Polymeric solutions - X-ray studies
Small and wide angle x-ray diffraction has been used in various characterizing various aspects of polymers such as the relationship between the structure and the mechanical properties [64]. WAXS has been used to elucidate the molecular structure of certain polymers [65], but sometimes this technique is used with other techniques such as optical microscopy [66] in order to understand complete understanding of morphology and other structural aspects of polymer.

8. DEVELOPMENTS IN TECHNIQUES
Various techniques are used in combination with other techniques in order to carry out comprehensive characterization and elucidate the overall structural and functional aspects of the polymeric solution [67-72]. Some of such studies had been shown in Table 4.

9. CONCLUSION AND FUTURE PROSPECTS
The continuous development of the modern process industries has made it increasingly important to have information about the properties of materials, including many new chemical substances whose physical properties have never been measured experimentally. This is especially true for polymeric substances. The design of manufacturing and processing equipment requires considerable knowledge of the processed materials and related compounds. Also for the application and final use of these materials this knowledge is essential [9]. Future prospects in the development of polymeric materials and to ensure their versatile usage in almost every field of life include following goals to be achieved:

- The properties of known polymeric solutions should be correlated with their chemical structure, the establishment of structure-properties relationships is quite vital.
- Advance methods for the estimation and/or prediction of the more important properties of polymers, in the solid, liquid and dissolved states; especially, in cases where experimental values are not to be found is highly recommended.
Table 4. Characterization of polymer solution by X-ray Diffraction and other miscellaneous techniques.

<table>
<thead>
<tr>
<th>Polymer solutions</th>
<th>Instruments being used</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Synchrotron WAXS and SAXS</td>
<td>Effect of crystallinity and orientation along the fiber was illustrated.</td>
<td>[64]</td>
</tr>
<tr>
<td>Thermotropic copolyester</td>
<td>Wide-angle X-ray scattering</td>
<td>The molecular behavior was correlated with viscoelastic properties.</td>
<td>[71]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Optical microscopy and synchrotron radiation(WAXD).</td>
<td>The morphology and crystalline structure changes of cellulose during dissolution in [(BMIM)Cl] were investigated in detail.</td>
<td>[72]</td>
</tr>
<tr>
<td>Hydrophobically modified alkali-soluble emulsion</td>
<td>Dynamic light scattering and rheological techniques</td>
<td>Common linear reduced viscosity plot down to extremely dilute concentration regime has been obtained.</td>
<td>[67]</td>
</tr>
<tr>
<td>Polystyrene chains</td>
<td>Fluorescence correlation spectroscopy (FCS) and dynamic light scattering (DLS).</td>
<td>Self-Diffusion and cooperative diffusion in semidilute polymer solutions had been investigated.</td>
<td>[69]</td>
</tr>
<tr>
<td>Blends of deuterated polystyrene and poly(vinylmethyl ether)</td>
<td>Rheology and in situ small-angle neutron scattering (SANS)</td>
<td>Study of structural changes in soft matter systems while exposed to shear gave vital information related to the dynamics of polymers.</td>
<td>[70]</td>
</tr>
<tr>
<td>Poly (ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), and poly(vinyl pyrrolidone) (PVP).</td>
<td>Capillary breakup extensional rheometry (CaBER)</td>
<td>The extensional properties of polymer solutions were effectively measured.</td>
<td>[71]</td>
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<td>Micellar solutions of cetyltrimethylammonium bromide (CTAB) and sodium p-toluene sulfonate</td>
<td>Rheology and small-angle neutron scattering (SANS)</td>
<td>The physical meaning of the anisotropic SANS patterns accompanied by shear-thickening flow behavior was discussed in detail.</td>
<td>[72]</td>
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REFERENCES


