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INVESTIGATION OF THE GENERAL PROPERTIES OF SOME POLYELECTROLYTE COMPLEXES

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BAZI POLİELEKTROLİT KOMPLEKSLERİN GENEL ÖZELLİKLERİNİN İNCELENMESİ

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ABBREVIATIONS

PEC : Polyelectrolyte complex

PMAA : Polymethacrylic acid

PSP : Poly(sodium phosphate)

P4VP : Poly(4-vinylpyridine)

PDMAEM : Poly(dimethylamino ethyl methacrylate)

PVPA : Poly(vinyl phosphonic acid)

P2VP : Poly(2-vinylpyridine)

PAMPSNa : Poly[sodium(2-acrylamido-2-methyl propane sulfonate)]

P4VPHCl : Poly(4-vinyl pyridinium chloride)

$4VPH^+$: 4-vinylpyrinium unit

DMA : N,N dimethyl acrylamide

PSS : Poly(sodium styrene sulphonate)

PAA : Poly(acrylic acid)

PEO : Poly(ethylene oxide)

PAMPS : Poly(2-acrylamido-2-methyl propane sulphonic acid)

TBuAH : Tetrabutyl ammonium hydroxide

DMSO : Dimethyl sulfoxide

DMF : N,N dimethyl formamide

PMMI : Poly(monomethyl itaconate

NaPES : Sodium poly(ethylene sulphonate)

PEEK : Poly(ether ether ketone)

PABA : 4-aminobenzoic acid

PABCl : 4-aminobenzoic acid, hydrochloride

P4VEBr : Poly(4-ethylpyridinium bromide)

PVP : Poly(vinyl pyrolidone)

XPS : X-Ray Photoelectron Spectroscopy

DSC : Differential Scanning Calorimetry

AAS : Atomic Absorption Spectroscopy

NMR : Nuclear Magnetic Rezonans

INVESTIGATION OF THE GENERAL PROPERTIES OF SOME POLYELECTROLYTE COMPLEXES

SUMMARY

Polyelectrolyte complexes, also called interpolymer complexes, are new class of chemically distinct and identifiable compounds. They are formed by polyelectrolytes that are macromolecules carrying a relatively large number of functional groups, or under suitable conditions can become charged. Polyelectrolytes interact with various low and high molecular weight substances and form interpolymer complexes. These complexes are either separated from the solution as solids (polycomplex salt) or may settle as a polyelectrolyte complex gel, and they can be soluble in solution by controlling experimental factors. They are, in general, obtained in either case, by mixing polyelectrolytes solution, and by matrix polymerization. Significant differences might exist between the chemical, thermal and mechanical properties of interpolymer complexes with respect to their components and experimental conditions. All biological macromolecules, proteins, nucleic acids, and polysaccharides are polyelectrolytes and interact with each other and small ions during their biological function. Their electrostatic interactions contribute a significant part of the structural stabilization of biological molecules and they are major determinants for the kinetics of biological process. Considering all these vital processes research on the polyelectrolyte complexes obtained by synthetic polyelectrolytes might be a simple model system for the complicated biopolymer reactions. Studying the special properties of polycomplex formation between synthetic polyelectrolytes and low molecular weight compounds can be useful for a understanding the nature of protein-lipid interaction in biomembranes or in the mechanism of protein denaturation. On the other hand, polyelectrolyte complexes are very promising materials for semi-permeable membranes for the industrial applications such as desalting of sea water, ultrafiltration and purification of aqueous solution and also for ultrafiltration of biological liquids.

With all the above given respects, numerous studies have been made successively on various polyelectrolyte complexes in the last two decades. However very few studies have been reported on the interaction between some certain polyphosphates and vinylpyridine polymers. One of a few studies with poly(phosphate) has been given by N. Acar and T.Tulun on the interaction of poly(sodiumphosphate) (PSP) and poly(4-vinylpyridiniumchloride) (P4VPHCl).The present study was aimed to

investigate the interaction between poly(sodiumphosphate) and poly(4-vinylpyridiniumchloride) with 4-amino benzoic acid (low molecular weight compound) individually as well as the detailed continuation of the previous work which dealt with the polyelectrolyte complex formed by PSP and P4VPHCl. Poly(sodium phosphate) is interesting because it is an inorganic polymer and, rather unusually it is one of the few anionic polymers of the integral type. Actually polyphosphates are somewhat analogous to the nucleic acids. Vinylpyridine polymers have particular importance as polyelectrolytes and have great ability to develop interpolymer complexes with polyacids.

The present study aims to form polyelectrolyte model complexes similar to or mimicking biologically active compounds and, thus, to understand the operating mechanism of biopolymers in living organisms through the investigation of the structure and various features of these model complexes.

In the experimental part of the study, insoluble polyelectrolyte complexes were obtained from the both, concentrated and dilute solutions of PSP and P4VPHCl. Stoichiometry of the isolated complexes were found to be 1:1 as a result of analysis of the supernatant liquid in conjunction with concentration of the initial components. In the dilute aqueous solution, occurrence of polyelectrolyte complex was proved by UV spectroscopy. Salt effect of NaCl, the effect of NaCl on complex formation and thermal properties of complexes were investigated.

Regarding the reaction of PSP with 4-amino benzoic acid, hydrochloride (PABCl), the stoichiometry of complex was found as 1:1.2 using viscometric and volumetric analysis of the supernatant. Besides, spectroscopic and conductometric methods were used for the complex stoichiometry. The experimental factors such as pH, ionic strength and temperature that affect the stoichiometry of complex were investigated. In the case of the poly(4-vinylpyridine) (P4VP) with 4-aminobenzoic acid, IR spectroscopy, potentiometry and DSC were used and the nature of binding between the components was identified as hydrogen bonding.

It is known that transition metals take part in the biochemical process. In the present study, interaction of copper (II) with P4VP- PABA complex system is of interest. Potentiometric method was used to follow the above stated interaction in aqueous ethanol solution for P4VP-PABA system. Protonation and the stability constants of P4VP-PABA system were determined.

Swelling properties of polyelectrolyte systems have been studied largely due to their industrial uses. In order to investigate the swelling properties of P4VPHCl-PSP system, PSP and P4VP that is the initial component of polycation were subjected to irradiation for six different radiation doses to obtain crosslinked structure. It is found that radiation has no affect on PSP. After irradiation the insoluble, the gel, parts were determined by soxhlet extraction and UV spectroscopy. Up to certain dose the gel percent of P4VP samples increased, and thereafter remained unchanged. From the relation between gel fraction and radiation dose, the efficiency of crosslinking and of scission were determined.

Irradiated P4VP that contained only gel part was quaternized to obtain water swellable P4VPHCl gel. The interaction of P4VPHCl gel with the aqueous solution of PSP was investigated considering ionic strength and pH.

BAZI POLİELEKTROLİT KOMPLEKSLERİN GENEL ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

İnterpolimer kompleksler olarak ta bilinen polielektrolit kompleksler kimyasal olarak farklı ve karakterize edilebilen yeni bir bileşikler grubudur. Polielektrolit kompleksler, nispeten çok sayıda fonksiyonel grup içeren ya da uygun koşullarda yüklü hale gelebilen makromoleküllerden, polielektrolitlerden, oluşur. Polielektrolitler düşük veya yüksek molekül ağırlıklı maddelerle reaksiyona girerek interpolimer kompleksleri meydana getirir. Bu kompleksler, çözeltiden katı (polikompleks tuzu) veya jel olarak ayrılabileceği gibi deneysel faktörler değiştirilerek çözelti içinde çözünür halde de bulunabilir. Genellikle polielektrolit çözeltilerinin birbirleriyle karıştırılması veya matriks polimerizasyonu ile elde edilen interpolimer komplekslerin kimyasal, termal ve mekanik özellikleri, deneysel koşullara da bağlı olarak, başlangıç bileşenlerinden oldukça farklı olabilmektedir. Bütün biyolojik makromoleküller, proteinler, nükleik asitler ve polisakkaritler polielektrolittir ve biyolojik fonksiyonlarını yerine getirirken birbirleriyle olduğu gibi küçük iyonlarla da reaksiyona girerler. Bunlar arasındaki elektrostatik etkileşimler, biyolojik moleküllerin yapısal kararlılığını sağlamada önemli bir paya sahiptir. Son derece önemli olan bütün bu prosesler düşünüldüğünde, sentetik polielektrolitlerle oluşturulan polielektrolit kompleksler üzerinde yapılan araştırmalar karmaşık biyopolimer reaksiyonlarını anlamaya yönelik basit modeller oluşturabilir. Örneğin sentetik polielektrolitler ve düşük molekül ağırlıklı bileşikler arasındaki polikompleks oluşum özelliklerinin incelenmesi, biyomembranlardaki protein-lipid etkileşimlerinin yada protein bozunma mekanizmalarının anlaşılmasına yardımcı olabilecektir. Polielektrolit kompleksler, deniz suyundan içme suyu elde edilmesi, biyolojik sıvıların yada sulu çözeltilerin ultrafiltrasyonu gibi birçok endüstriyel alanda kullanılan yarı geçirgen membranlar için de çok ümit verici malzemelerdir.

Yukarıda belirtilen nedenlerle son yirmi yıl içinde, polielektrolit kompleksler üzerinde, ardarda çok sayıda çalışma yapılmıştır. Ancak, literatürde poli(vinilpiridin)ler ile belirli polifosfatlar arasındaki etkileşimlerle ilgili birkaç çalışma bulunmaktadır. Poli(sodyum fosfat) (PSP) ile poli(4-vinil piridinyum klorür) (P4VPHCl) arasındaki etkileşimi inceleyen birkaç çalışmadan biri N.Acar, T.Tulun tarafından verilmiştir. Mevcut çalışmada, PSP ve P4VPHCl'nin 4-amino benzoik asit (PABA) ile ayrı ayrı reaksiyonların incelenmesi ve poli(4-vinil piridinyum klorür)

(P4VPHCl) ile poli(sodyum fosfat) (PSP) arasındaki polikompleks oluşumuyla ilgili olarak önceki çalışmanın detaylandırılarak daha ileri götürülmesi amaçlanmıştır. Polifosfatlar iyonik gruplarını ana zincir üzerinde bulunduran birkaç anyonik anorganik polimerden biri oluşu ve nükleik asitlere benzer yönleri olmaları nedeniyle oldukça ilgi çekmektedirler. Diğer yandan poli(vinil piridin)ler poliasitlerle interpolimer kompleks oluşturma özelliğine sahiptir. Ayrıca, kompleksin herbir bileşeninin 4-amino benzoik asit ile olan reaksiyonları ilgi çekicidir, çünkü amino asitler proteinlerin yapısındaki temel elemanlarındandır.

Bu çalışmada, biyolojik aktiviteye sahip bileşiklere benzetilebilecek polielektrolit kompleks yapılması, bu komplekslerin yapısının ve çeşitli özelliklerinin ortaya koyularak elde edilebilecek bu model bileşik yardımıyla canlı mekanizmalardaki çeşitli biyopolimerlerin etki mekanizmalarının incelenmesi amaçlanmıştır.

Çalışmanın deneysel kısmında, derişik ve seyreltik PSP, P4VPHCl çözeltilerinden çözünmeyen polielektrolit kompleksler elde edilmiştir. Elde edilen komplekslerin stokiyometrisi süzüntü analizleri sonucunda 1:1 olarak bulunmuştur. Seyreltik çözeltide polielektrolit kompleks oluşumu UV spektroskopisi ile gösterilmiştir. Kompleks oluşumuna NaCl etkisi, kompleksin parçalanması ve termal özellikleri de incelemiştir.

PSP ile 4-amino benzoik asit, hidroklorür (PABCl) arasındaki reaksiyonda ise kompleks stokiyometrisi viskometrik ve süzüntülerin volumetrik analizleri sonucunda 1:1.2 olarak bulunmuştur. Ayrıca kompleks stokiyometrisi için spektroskopik ve kondüktometrik yöntemler kullanılmıştır. pH, iyonik şiddet ve sıcaklık gibi kompleks stokiyometrisini etkileyen deneysel faktörler incelenmiştir. Poli(4-vinil piridin) (P4VP) ile 4-amino benzoik asit durumunda, IR spektroskopisi, potansiyometri ve diferansiyel taramalı kalorimetri (DSC) yöntemleri kullanılmış ve iki bileşen arasında hidrojen bağı oluştuğu ileri sürülmüştür.

Geçiş elementlerinin biyolojik proseslerde yer aldığı bilinmektedir. Bu çalışmada Cu(II) iyonlarının P4VP-PABA kompleks sistemi ile etkileşimi potansiyometrik yöntemle incelenmiştir. Cu(II) iyonlarının P4VP-PABA sistemi ile olan reaksiyonlarında sulu ethanol çözeltileri kullanılmıştır. P4VP-PABA sisteminin protonasyon ve stabilite sabitleri tayin edilmiştir.

Polielektrolit kompleks sistemlerin şişme özellikleri endüstriyel alandaki uygulamaları nedeniyle oldukça fazla çalışılmaktadır. P4VPHCl-PSP sisteminin şişme özelliklerini incelemek için, PSP ve P4VP radyasyona uğratılarak çapraz bağlı yapılar elde edilmeye çalışılmış, ancak radyasyonun PSP üzerinde etki yapmadığı bulunmuştur. Bu çalışmada kullanılan, başlangıç bileşeni olan P4VP vakum ortamında altı farklı dozda radyasyona maruz bırakılmıştır. Çözünmeyen, jel, kısım UV spektroskopisi ve soxlet ekstraksiyonları ile saptanmıştır. Belirli doza kadar jel yüzdesi artmış, daha sonra sabit kalmıştır. Çapraz bağlanma ve bölünme verimleri, jel fraksiyonu ile radyasyon arasındaki bağlantıdan yararlanılarak bulunmuştur.

Çapraz bağlı P4VP kuaternize edilerek, suda şişme özelliğine sahip P4VPHCl jelleri elde edilmiştir.Son olarak, iyonik şiddet ve pH dikkate alınarak P4VPHCl jeli ile PSP çözeltileri arasındaki kompleks oluşum reaksiyonu da incelenmiştir.

CHAPTER 1. INTRODUCTION

During the recent years, studies on the interpolymer complexes are of importance with respect to industrial application and vital processes occurring in biological systems. Interpolymer complexes are very promising materials for semi-permeable membranes that are used for the desalting of sea water, for ultrafiltration in concentration of water solutions containing micro and macroparticles and of biological liquids. They have also potential applications as microcapsules and medical implants. As a scientific point of view considering that all biopolymers such as proteins and nucleic acids are polyelectrolytes, complexation between two synthetic polyelectrolytes might provide a simple model system for complicated biopolymer reactions. Particularly, polyelectrolyte complex formation between synthetic polyelectrolytes and low molecular weight compounds can be useful for a global understanding the nature of protein-lipid interaction in biomembranes or in the mechanism of protein denaturation.

Significant differences exist between the physical, chemical, thermal and mechanical properties of interpolymer complexes with respect to those of their components. The first study on this area was reported in 1949 for the poly(vinyl-N-butyl pyridinium bromide), poly(styrene sulfonate) system. However, polymer complexes have been actively studied since Michaels et al [1] reported the formation, properties and possibility of various applications of interpolymer complexes. Since then, different kinds of interpolymer complexes have been studied extensively. The numerous studies made successively on this area are outlined in Chapter 2. The present study was aimed to investigate the interaction between poly(sodium phosphate) and poly(4-vinylpyridinium chloride) with 4-aminobenzoic acid (low molecular weight compound) individually as well as the detailed study of the polyelectrolyte complex formation between poly (sodiumphosphate) and poly(vinylpyridinium chloride). In order to investigate the swelling properties of the complexes, poly(vinylpyridine), which is the precursor of polycation, was necessarily irradiated to increase the

crosslinked structure. Therefore, a review of the exhaustive studies on this area is given in Chapter 2, in order to elucidate insights of the previous work to benefit for the present study. In Chapter 3, the objectives of the work and the reasons of selection of polymers are outlined. Experimental methods utilised throughout the study are described in Chapter 4. Evaluation and discussion are presented in Chapter 5. Lastly, the main conclusions drawn from the results and the related discussions are briefly summarised in Chapter 6.

CHAPTER 2. THEORETICAL PART

Interpolymer complexes have already been known for a long time on an emprical basis from the mutual precipitation of proteins. At the end of 19th century Kossel [2] recognised the electrostatic nature of the interaction between oppositely charged polyions. However, major developments in this area began in 1960's when Michaels succeeded in preparing well-defined 'polysalt', with a 1:1 stoichiometric ratio of anionic to cationic charges, from oppositely charged vinyl based polycation and poly(styrene sulfonate). Further landmarks in this development phase can be gathered under three distinct titles as in the following;

1. Preparation and characterisation of soluble polyanion-polycation complexes by Tsuchida [3] and Kabanov [4].

2. The synthesis and quantitative description of polyelectrolyte complexes between synthetic and natural polymers.

3. The investigation of polyelectrolyte–surfactant complexes into the field of interpolymer complexes.

As our understanding has matured parallel to the research efforts and accomplishments, polymer complexes have found numerous areas of application and there are still a large number of works in progress to exploit the desirable properties of interpolymer complexes and put them in application in diverse field.

This chapter covers the detailed discussion and main outcomes of these studies. Section 2.1 describes the basic concept of polyelectrolytes. Basic methods for obtaining interpolymer complexes and the techniques applied for the investigation of complex formation and structure are discussed in Section 2.2. In Section 2.3 interpolymer complexes are classified. In section 2.4 the formation of polyelectrolytes from synthetic and natural polyelectrolytes are discussed. The

effects of the reaction conditions on polyelectrolyte complex formation are also explained in this section. Another class of interpolymer complexes, hydrogen bonding complexes, and the factors affecting their formation are given in Section 2.5. To show the importance of research on polymer complexes from both scientific and practical point of views, properties and applications of interpolymer complexes are presented in Sections 2.6 and 2.7, respectively. The following two sections, 2.8 and 2.9, discuss the general properties of poly(vinyl pyridines) and poly(phosphates) that were selected as the component polymers to form polymer complexes in the present study.Finally, the advantages of radiation technique and the factors affecting on the radiation resistance of polyions are discussed in Section 2.10.

2.1. Polyelectrolytes

Polyelectrolytes are polymers possessing many ionizable groups. The combination of polymeric and electrolyte behaviour gives them a number of useful properties. Polyelectrolytes may be biological in origin such as nucleic acids, or may be synthetic. Polyelectrolytes may be classified as anionic, cationic or ampholytic, according to whether the ionized polymer carries negative charges, positive charges or both. Polyelectrolytes are generally soluble in water [5].

Repulsion between charged groups on the polymer leads to a flexible polyelectrolyte being more expanded than an equivalent nonionic polymer. At low concentrations in pure water, a polyelectrolyte may be almost rod-like. If a simple salt is added to the solution, the charges on the polymer are to some extent shielded from each other and the degree of expansion decreases [6].

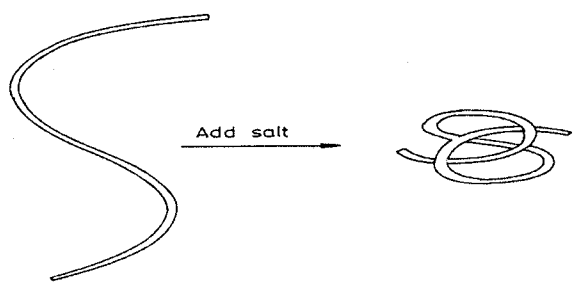


Figure 2.1. Effect of a salt on the degree of expansion of a polyelectrolyte chain.

For a weakly acidic or basic polyelectrolyte, dimensions of the polyions can be strongly dependent on the degree of neutralization. The electrical and electrochemical properties of polyelectrolyte solutions are different from analogous low molar mass electrolyte solutions [6].

2.2. Methods For Obtaining Interpolymer Complexes

There are two main methods for obtaining interpolymer complexes;

1) Matrix polymerization

2) Formation of complexes from pre-existing chemically and structurally complementary macromolecules.

2.2.1. Matrix Polymerization

Polymerization of monomers in the presence of polymers which can interact with monomers is called matrix polymerization or template polymerization. Matrix polymerization is a two step process. The first one involves the reaction between a charged polymer and an oppositely charged monomer whereas second one involves the polymerization of the monomer. It is expected that matrix polymerization fundamentally controls some structural details for example, molecular weight, isomerism, etc. Up to now, many works on matrix polymerization have been reported. Blumstein et al. [7] prepared highly ordered polyelectrolyte complexes through matrix polymerization and it was the first report of one synthetic polymer serving as a template for the ordered growth of another type of synthetic polymer. Cerrai et al. [8] showed the polymerization of acrylic acid and sodium 4-styrenesulfonate in the presence of chitosan as a template gives insoluble products, identified as the polyelectrolyte complexes. They also reported formation of an amorphous polyelectrolyte complex by polymerization of sodium acrylate onto polyallylamine hydrochloride and determined its physicochemical properties [9] Kabanov et al. [10] obtained crystalline polyelectrolyte complex by using 4-vinylpridine and isotactic poly(acrylic acid).

2.2.2. Formation of Interpolymer Complexes

Polyelectrolytes are obviously the most suitable materials for the investigation of the chemical interactions between macromolecules. The products of the reactions between chemically complementary polymers, i.e. polymers whose functional groups have an affinity for one another are called interpolymer complexes or polycomplexes. Interpolymer complexes that would be regarded as a special class of polymeric compounds, particularly for their being to exist in dilute aqueous solution.

One of the important properties of interpolymer complexes is their ability to enter into interpolymer exchange and substitution reactions in aqueous solutions.

2.2.3. Methods Applied for the Investigation of Complex Formation and Structure

Different methods can be used to investigate the formation and composition of interpolymer complexes.

Conductometric measurement of counterion liberation during interpolymer complex formation can be applied to all systems in question to determine an electrochemical end point, and hence the stoichiometry of the reaction. A limitation is given by the decrease in sensitivity in the presence of large amounts of low molecular weight electrolytes.

Application of potentiometry to indicate an electrochemical endpoint in complex titration is mainly employed in connection with polyacid- polybase systems or to systems with one component bearing a free polyacid or polybase. Potentiometry in some cases has also yielded additional information on counterion concentration, especially of halide ions in the liquid phase after interpolymer complex precipitation.

The experimental results may be represented both by titration curves or property-composition dependences. The extremums or bends on titration curves indicate the formation of complexes and their compositions.

Turbidimetry is a valuable tool applicable to all systems for determining a "turbidimetric endpoint", not necessarily coinciding with electrochemical one.

Results can be drawn from the form of the turbidimetric curve. Sedimentation measurements in the ultracentrifuge can yield data on polycomplex aggregates as well as on residual free polymer in combination with other methods.

Spectroscopic techniques are of special importance for approaching problems of preferential binding in a limited number of suitable systems and for obtaining information an conformational changes, especially in systems containing proteins.

For assessing the molecular composition of isolated polycomplex, classical elemental analysis is still to be considered a most important technique, requiring no additional assumptions or special preparation. An elimination of low molecular weight salts by washing or dialysis must be done to obtain reliable stoichiometric data by this method.

The use of solid state NMR for assessing supermolecular structure of solid polycomplex is not very widespread.

Morphological investigations on precipitated polycomplexes by electron microscopy are often impeted by preparation problems.

2.3. Types of Interpolymer Complexes

Interpolymer complexes can be divided into several types, depending on the kind of the dominating interaction:

1) Polyelectrolyte complexes (PEC) are formed by mixing oppositely charged polyelectrolytes, i.e. polyanions and polycations, due to Coulombic forces. Simultaneously, microions are released almost quantitatively.

2) Hydrogen-bonding complexes between polyacids and water soluble nonionic polymers stabilized by hydrogen bonds.

3) Charge transfers complexes are formed in systems of electron accepting polymer and electron donating polymers through charge transfer interactions.

2.4. Polyelectrolyte Complexes (PEC)

Oppositely charged polyelectrolytes interact with each other to form polyelectrolyte complexes (PEC). They are divided into four subclasses by a combination of strong and weak polyelectrolytes [11]. Considering that all biopolymers are polyelectrolytes studies on PEC of synthetic macromolecules as models of complicated biological systems are very important [12]. The formation of PEC is governed by the characteristics of the individual polyelectrolyte components, e.g. strength and position of ionic sites, charge density and rigidity of polymer chains, as well as the chemical environment, such as solvent, pH, temperature and concentration [13]. Significant differences exist between the mechanical and thermal properties of PEC with respect to those of their components due in part to the crosslinked nature of PEC [14-16]. PEC are either separated from the solution as solids or liquids or they are still soluble in solution or may settle as gels [17-19].

2.4.1. PEC Between Two Synthetic Polyelectrolytes

Comprehensive investigations on formation, structure and potential applications of PEC between sodium salt of poly (styrene sulphonic acid) and poly(vinylbenzyltriammonium chloride) have been performed by Michaels and his group [1,11]. By conductometric and turbidimetric titrations as well as by elemental analysis of the precipitates, Michaels et al. showed a 1:1 stoichiometry on this kind of PEC formation. His arguments for 1:1 stoichiometry were based on conductometric results obtained with the sodium and the halide salts of the components at low concentrations. He also reported the deviation from 1:1 stoichiometry in the presence of low molecular weight electrolytes. It was established that the precipitate was insoluble in any of the known particular solvents. Admittedly it was possible to dissolve it in ternary systems of the acetone-water-NaBr type, but this process took place as a result of the decomposition of the complex. The combination of insolubility in familiar simple solvents with a high swellability in water, selectivity in the sorption of ions, and high biological compability have led to the application of such complexes as material for medical-biological purposes.

The procedure used to obtained water soluble PEC was first described in detail by Tsuchida et al. [3]. It consisted of mixing aqueous solutions of aromatic ionenes and sodium polystyrene sulphonate (NaPSS) in non-equivalent proportions. The complete dissolution of the PEC was observed in the presence of a three-fold excess of the charged units of ionene. After the introduction of excess amount ionene into a solution of sodium poly(styrene sulphonate), an insoluble stoichiometric PEC was obtained instead of the non-stoichiometric one, while the excess ionene remained in solution. Tsuchida et al. concluded that the polymers of the ionene series had a special capacity for the formation of water soluble PEC. This conclusion was confirmed by Gulyaeva et al. [20]. It was shown that the reaction between sodium polyacrylate and 5,6 ionene bromide that aliphatic ionenes were also capable of forming water soluble PEC.

Tsuchida et al. [21,22] investigated the PEC formation by potentiometric and conductometric titrations at different degrees of conversion of reacting polyacids and polybases. When a weak polyacid or a weak polybase was used as the polyelectrolyte component, the dissociation state of the weak polyelectrolyte directly affected the complexation ability and the composition of the complex obtained. The results of his studies showed that the yield of PEC obtained was proportional to the amount of each polymer component added. Furthermore, even when the degrees of polymerization of two polymer components differed identical phenomena observed.

Tsuchida also calculated thermodynamic constants of complex formation and complex stability, giving special regard to the influence of the molar mass of one of the components by employing a series of oligomeric linear poly(ethyleneimine) samples [23].

Comprehensive contributions to PEC stoichiometry have been published by Kabanov et al. [24-27]. It was shown that water-soluble complexes obtained at certain conditions from polyelectrolytes having a wide variety of chemical structures. It was established that non-stoichiometric PEC formed in acid media in the reaction of polymethacrylic acid (PMAA) with poly (N-ethyl-4 vinylpyridinium bromide) were insoluble in water. The addition of alkali leaded to the ionization of the free carboxy-groups of the PMAA and to the dissolution of the non-stoichiometric PEC [25].

In connection with his investigations on soluble complexes, Kabanov also performed experiments on complex stoichiometry by potentiometric back titrations of liberated counterions. These results have been also used for thermodynamic calculation on complex stability.

Tsuchida et al. titrated polymethacrylic acid, PMAA, potentiometrically in the absence and presence of polycations and their low molecular weight analogs. In the presence of polycations, the pH of the PMAA aqueous solution was remarkably lowered. This was caused by the release of protons accompanied by the formation of polyelectrolyte complexes. On the other hand, in the presence of low molecular weight analogs, the pH changes only slightly, which meaned that a stable complex was not formed. From this result it can be supposed that the chain length of the polymer component is one of the factor for the control of the complex formation.

In order to describe the molecular weight effect, Kharenko et al. [28] studied the complex formation between poly (dimethylaminoethylmethacrylate) (PDMAEM) and polyphosphate. They found that the critical degree of polymerization polyphosphate in reaction with PDMAEM in salt free media was 7. This was 20 times less than the critical degree of polymerization of poly (ethylene glycol) forming a complex with PMAA.

When the pH of the solution, (i.e. the degree of neutralization) of a weak polylectrolyte complex is changed, the composition of the polyelectrolyte complex can change. The pH dependence of the complexation ability of the systems of poly (vinylpyridine) and poly(glutamic acid) was investigated by Tsuchida et al. [29]. In these systems, only in the neutral pH region, both weak polyelectrolytes could partially dissociate and complex was formed. However, at higher or lower pH, the complex was not formed because the degree of dissociation of either the weak polyacid or the weak polybase was relatively low.

Izumrudov et al. [30] reported non-equimolar water-soluble polyelectrolyte complexes composed of PMAA and quaternized poly (4-vinylpyridine) (P4VP). In acid media composition of PEC was equal to a ratio of [PMAA]: [P4VP]=5:1 (PEC 5:1). They showed that titration of PEC (5:1) with alkali resulted in complete dissolution of PEC. At pH 4,5 majority of P4VP units had formed salt bonds with

carboxylate-anions of PMAA, so that a further rise in pH resulted in charging of –COOH groups of PMAA in excess in the polycomplex and was not linked by salt bonds to polybase chains and complete dissolution of PEC took place.

In order to describe the steric effect on complexation, Zhou et al. [31] studied the interaction between poly(vinylphosphonic acid) (PVPA) with poly(4-vinylpyridine) (P4VP) and with poly(2-vinylpyridine) (P2VP). Mixing of polymer solutions led to the formation of insoluble complexes. They used X-ray photoelectron spectroscopy (XPS) to characterize complexes. They showed that the pyridine groups in P4VP and P2VP in the complexes had been protonated. The extent of the protonation of the pyridine groups was estimated from the peaks of XPS spectra. They found that the fraction of protonated pyridine groups increased linearly with increasing PVPA content in the complex. The fraction of protonated pyridine groups was higher in the PVPA/P4VP complex than in the PVPA/P2VP complex. Such a behaviour confirms with the general view that the nitrogen in P4VP was more accessible than that in P2VP due to steric effects.

Huglin et al. [32,33] prepared PEC by mixing aqueous solutions of oppositely charged polyelectrolytes poly[sodium(2-acrylamido-2-methyl propane sulfonate)] (PAMPSNa) and poly(4-vinylpyridinium chloride)(P4VPHCl). PEC compositions were determined from elemental and UV analysis of supernatant liquids. They explained the departures from 1:1 stoichiometry were probably due to the existence of unreacted moieties in PEC. They found that PEC contained an excess of vinylpyridinium groups. An excess cationic groups in PEC had also been noted by Fuoss and Sadek [34] in their study on PEC from mixing aqueous solutions of poly(vinlybutylpyridinium bromide) and poly(sodium styrene sulfonate). Huglin et al.[35] considered the basic strength of the pyridine group in the poly(4-vinylpyridine) homopolymer to explain excess of caitonic groups in the PEC. The pKa of poly(4-vinylpyridine) in water was 4.2 at 298 K and the complete protonation of poly(4-vinylpyridine) in water was difficult to achieve. The unprotonated groups did not form ionic crosslinks with sulfonate moieties and, in order to retain electrical neutrality, unreacted AMPS$^-$(2-acrylamido-2-methyl propane sulfonate) groups in the PEC remained bound to sodium counterions.

Formation of polyelectrolyte complexes is mainly affected by the charge density of the components. Huglin et al [36] inserted neutral spacers N, N dimethyl acrylamide (DMA) in the chains of one of the precursors to investigate the influence of charge density on PEC reaction stoichiometry and precipitate compositions. They concluded that reducing the charge density of the polyanionic component by the addition of neutral spacer interactions facilitated between oppositely charged groups.

Kudaibergenov et al. [37] studied the formation of complexes between linear or crosslinked poly[4-(but-3-en-1-ynyl)-1-methylpiperidin-4-ol] (polybase) and linear as well as crosslinked poly(acrylic acid) (polyacid) by conductometry, potentiometry, turbidimetry and viscometry. They showed the potentiometric and conductometric titrations of polybase with polyacid in different molar ratios ([polybase]:[polyacid]). Titration curves showed two bends corresponding to the stoichiometry [polybase]: [polyacid] 1:1 and non-stoichiometric PEC [polybase]:[polyacid] 2:1. The formation of two types of PEC could be explained by the conformational state of polybase. The formation of non-stoichiometric PEC took place at pH>5 and polybase had a compact structure at this pH. Further addition of polyacid induced the expansion of the polybase, so additional binding of carboxylic groups of polyacid occured and composition of PEC becomed stoichiometric.

Mustafayev et al. [38] determined the interaction between poly(4-vinylpyridine) and bovine serum albumin in an acidic medium, and participation of bivalent copper ions in that interaction had been investigated. They formed a soluble ternary complex over a wide range of the ratio between components.

An attempt was made by Ferguson et al. [39] to gain better understanding of the complexation between poly(acrylic acid) and poly(vinylpyrolidone), and the influence of the presence of Cu^{2+} ions in aqueous and ethanol-aqueous solutions. It was found that the rate of complexation was enhanced in the presence of Cu^{2+} ions, also it was more pronounced in water than in an ethanol-water solution.

Glass transition temperature (T_g) of polymer is related to the its chemical structure [40]. In general, factors that increase the energy required for the onset of molecular motion increase T_g [41, 42] that decrease the energy requirements lower T_g [43-45]. T_g is also governed by the presence and absence of crosslinks [46-48].

Goh et al. [49] determined T_g value of P4VP as 408 K. Insoluble interpolymer complexes were obtained between P4VP and poly (vinylphosphonic acid) and T_g values of complexes were compared with T_g value of initial polymers.

Katime et al. [50] found that P4VP exhibited a well defined glass transition. They obtained interpolymer complexes of poly (monomethyl itaconate) (PMMI) with P4VP. They reported that T_g of the complexes appeared at higher temperatures than that of pure P4VP. Higher in T_g' s were attributed to the possible morphology differences between complexes and initial polymers.

2.4.1.1. The Effects of The Reaction Conditions on PEC Formation

Reaction conditions for example, ionic strength, solvent, concentration of components and temperature affect the formation of polyelectrolyte complexes. When increasing the ionic strength, the following phenomena are expected to be observed:

1) Reduction of electrostatic interactions between polyions due to the screening effect of microsalts.

2) Acceleration of dissociation of weak polyelectrolytes owing to the decrease of intramolecular electrostatic repulsion.

Tsuchida et al. [13,17] showed the effect of ionic strength on viscosity and transmittance of the mixed aqueous solution of PMAA (weak polyacid) and integral type polycation (strong polybase). In dilute solution, the complex was formed whereas in concentrated systems and at low pH, complex was not formed because of suppression on the dissociation of PMAA. The complex was dissociated into the corresponding polyelectrolyte components at 0.7 $molL^{-1}$ NaCl, because of the screening effect of microsalts.

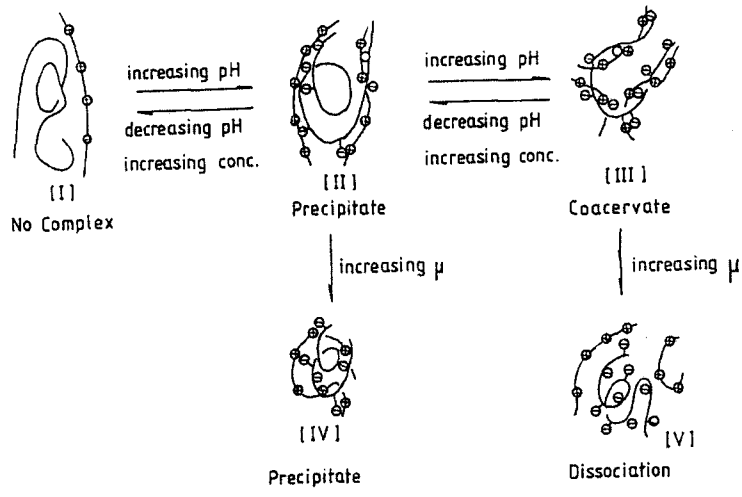


Figure 2.2. Schematic representation of the phase changes of the polyelectrolyte complex (From Ref. [13]).

They showed the changes of polyelectrolyte complex composed of a weak polyacid, PMAA, and a strong polybase schematicly. PMAA cannot dissociate at extremely low pH and very high concentrateions. Under this conditions they did not obtain the complex, because the amount of dissociated carboxylate anions was insufficient for the generation of a stable complex. On increasing either the pH or ionic strength or upon dilution, PMAA formed a stable complex with polycation, provided the amount of carboxylate anionic sites exceeded a certain critical value. Further increase of ionic strength enhanced the contraction of the polymer chain and the complex yield increased. When a large amount of microsalt was added to the system, the complex was broken.

Tsuchida et al. [17] also found that, the dependence of the viscosity in the complex upon temperature was different from the component polymers.

Huglin et al. [33] investigated the limiting salt concentrations required to suppress PEC formation between PAMPSNa and P4VPHCl. They used LiF, $NaClO_4$, NaSCN, NaBr, NaCl to show the prevention of PEC formation by the nature of the salt. Qualitative tests showed that precipitation occured upon mixing dilute aqueous of P4VPHCl with solutions of NaCl, NaBr, LiBr.

Itoh et al. [51] reported PEC formation of PAMPS and poly(sodium styrene sulphonate) (PSS), containing anthryl probes. They obtained that, PEC were

dissociated into the component polyelectrolytes at higher ionic strength for more than 0.7 $molL^{-1}$ of NaCl.

Effect of the type of cation on characteristic of poly(acrylic acid) (PAA)-ionene complex at pH 8 and in the presence of 0.025 $molL^{-1}$ NaCl and KCl was reported by Kharenko et al. [52]. They found that by replacing Na^+ counterion by a K^+ counterion, which was less strongly combined with the COO^- group of PAA chain, PEC was dissociated.

Schnabel et al [53] dealt with the ionic strength dependence of the stability of PEC from poly(N-ethyl-4-vinylpyridinium bromide) and poly(sodium methacrylate). It was shown that the formation of PEC was a reversible process as far as weak polyelectrolytes were concerned. The precipitated PEC from a solution of relatively low ionic strength was resolubilized upon increasing the ionic strength of the solution by the addition of a low molecular salt. Resolubilization took place at a certain critical ionic strength.

Izumrudov et al. [54] titrated the solutions of PEC (PAA-ionene) with LiCl, NaCl, KCl and $(CH_3)_4NCl$ solutions turbidimetrically. They showed that the type of anion had pratically no effect, and the solubility of PEC in dilute solution increased in the order: LiCl<NaCl<KCl<$(CH_3)_4$ NCl which was the same sequence of decrease in the constant of combination of a low molecular weight cation with a carboxyl anion.

2.4.2. PEC Between A Synthetic and A Natural Polymer

The interaction between bovine serum albumin and 4-vinylpyridine and 4-vinyl-N-cetylpyridinium bromide was investigated as a function of the length of the macromolecule [55-57]. It was shown that complexes formed by bovine serum albumin and polymer-analogues of poly(4-vinylpyridine) exhibited exceptionally high immunogenous properties. Mustafayev et al. [38] determined the interaction between poly(4-vinylpyridine) and bovine serum albumin in an acidic medium, and participation of bivalent copper ions in that interaction had been investigated. They formed a soluble ternary complex over a wide range of the ratio between components.

Vishalakshi et al. [58] studied PEC involving carboxy methylcellulose. They reported studies on the complex formation between carboxymethylcellulose and quaternized poly(2-vinylpyridine) and poly(4-vinylpyridine). Molecular weight of the polycations, concentration of the polyions on the stoichiometry of the complex was reported. They found that the molecular weight of the polycations did not have any influence on the chemical composition of the precipitate .

The complex formation is considered to cause a confirmational change of polyelectrolyte chains. Interpolymer complex formation between poly(proline) with helical structure and a polyacid in an aqueous solution have been studied by Park et al. [59]. Formation of the complex was shown by the decreases in reduced viscosity of the solution on addition of an increasing quantity of poly(proline) to a constant amount of polyacid. An X-ray diffraction pattern for the complex gave no diffraction patterns which appeared in pure poly(proline), indicating the destruction of the helical structure of poly(proline) due to the interpolymer complexation.

In literature qualitative observations on the precipitation of proteins or precipitation of a protein with a polysaccharide are mentioned. Complex stoichiometry in system consisting of two natural polymers or their ionic derivatives shows large deviations from 1:1 stoichiometry [60-62].

2.5. Hydrogen Bonding Complexes

Proton-accepting polymers and proton-donating polymers interact with each other in aqueous medium or in organic solvents almost stoichiometrically. Many intermacromolecular complexes governed through hydrogen bonds occur in biological systems. However, complexes between synthetic polymers are limited to only a few systems consisting of proton-donating and proton-accepting polymers. As nucleic acid models, many studies have also been made on interactions between synthetic polymers containing nucleic acid bases. Formation of hydrogen bond containing complexes is affected by temperature, polymer structure, polymer concentration and solvent. In general, the ratio [proton-accepting polymer units]/[proton donating polymer units] in $molL^{-1}$ of the complex is almost unity in dilute solution.

2.5.1. Effect of pH on Hydrogen Bonding Complexes

Using poly(carboxylic acid) as a proton donating polymer, the complexation strongly depends on the pH of the aqueous solution, i.e. on the degree of dissociation of poly(carboxylic acid). Tsuchida et al. investigated the complex formation between PMAA and poly(ethylene oxide) (PEO). They found that dissociation of poly(carboxylic acid) was suppressed in the presence of PEO. From specific viscosity and pH mesaurements of the mixed solution of PMAA and PEO it was found that there was a critical state of dissociation called "critical pH".

The existence of a certain number of undissociated carboxy group was necessary to form a stable complex through hydrogen bonds. If this condition was satisfied at a certain pH (critical pH), a stable complex was formed irreversibly. The critical pH depends on the dissociation constants, pKa, of poly(carboxylic acids) [63, 64].

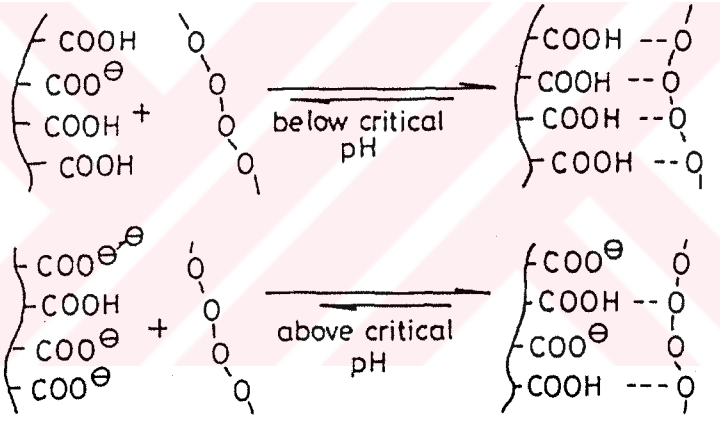


Figure 2.3. Effect of pH on the formation of polymer complex through hydrogen bonds in poly (methacrylic acid) – poly (ethylene oxide) system (From ref.[13]).

Kabanov et al. obtained a complex through hydrogen bonds between on mixing aqueous solutions of poly(methacrlic acid) and poly(acrylamide) followed by acidification of the solution to pH ~2 by adding 0.4 N HCl solution. It was reported chemical changes occured in complex in solid phase under heating [65].

The structure of polymer complexes stabilized through hydrogen bonds can be much influenced by the presence of nonactive groups on the polymer chain. Iliopoulos et

al.[66] investigated the complex formation between poly(acrylic acid) and poly(vinylpyrolidone). Partially neutralized groups of poly(acrylic acid) could not form hydrogen bonds and behaved like inactive groups. The potentiometric study of such systems showed that the presence inactive groups largely influenced the formation and the stoichiometry of the complex .

Monal et al. [67] analyzed the interpolymer reaction between poly(acrylic acid) and poly(vinylpyrolidone) by means of conductimetry and viscometry. Conductimetry was shown to be a useful tool in the investigation of this kind of complex because the polyacid dissociation was suppressed in the presence of poly(vinylpyrolidone). Near to stoichiometry there was a minimum in the viscosity-composition curves due to the formation of complex. When varrying the degree of neutralization of the polyacid to values lower than 0.1 a different behaviour was seen with respect to the composition of the complex .

The complex formation between poly(vinylether) of ethylene glycol and poly(acrylic acid) was studied using viscometric and spectroturbidimetric methods by Mun et al. [68]. They found that the addition of aqueous solution of poly(vinylether) of ethylene glycol to aqueous solution of poly(acrylic acid) in weakly acidic media (pH ~4-5) did not lead to the formation of complex and was accompanied to by increase in the intrinsic viscosity. This increase could be attributed to the presence of the polyelectrolyte effect. In acidic media (pH=2) the viscometric and turbidimetric curves showed minimum and maximum due to the complex formation. They have also checked the influence of ionic strength on the complex formation. In the presence of NaCl in solution, the turbidimetric curve and characteristic composition of complex deviated from the curve obtained without the salt. The yield of complex increased in the presence of NaCl. Ionic strength influenced the critical pH value for the system. The increase of ionic strength of the solution shifted the critical value to higher pH region.

Fujimori et al. [69] obtained a 1:1 hydrogen bonded complex between acrylic acid or methacrylic acid and the pyridine group of poly(4-vinylpyridine) in dilute solutions. A shift of infrared absorption of the hydrogen-bonded acid to a lower energy direction and shift of acid proton in the NMR were observed when the monomers

were added with pyridine. The equilibrium constants for acrylic acid and methacrylic acid complexed with the poly(4-vinylpyridine) were determined potentiometrically.

Budtova et al. [70] investigated the formation of interpolymer complexes on the surface of crosslinked poly(acrylic acid) with linear poly(vinlyalcohol). They added NaOH to solutions of the investigated mixture and no complex formation occured. When poly(acrylic acid) was ionized, no complex formation took place which showed that interpolymer complex formation occured due to hydrogen bonding of undissociated COOH groups of poly(acrylic acid) with hydroxylic groups of poly(vinylalcohol).

2.5.1. Effect of Solvent and Temperature

The possibility of complex formation has been observed not only in water, but also in some organic solvents. The complex formations of poly(acrylic acid)-poly(vinylpyrolidone) in methanol and poly(methacrylic acid)-poly(vinylpyrolidone) in DMF were investigated [16]. The composition of the complexes in these solvents was determined by conductometric and potentiometric methods. The titration curves in methanol, DMF and DMSO exhibited a typical inflection point termining the molar ratio of components in the complex. The complex compositions in organic solvent and water were different. The solvent, DMSO strongly competed for hydrogen bonds and the complex was broken down.

Bimendina et al. [71] investigated the complex formation in poly(vinylpyrolidone) and poly(itaconic acid monomethyl ester). Data of conductometric, potentiometric and viscometric titrations showed that complexes of equimolar composition were formed. The influence of an organic solvent (DMSO) on the stability of complexes also studied. The complexes were destroyed at DMSO content about 30-40 vol. % which followed from the increase of intrinsic viscosity values. Temperature dependence of the viscosity of complexes in water showed that their stability depended on molecular weight of poly(vinylpyrolidone). The complexes were destroyed on heating. The destruction was more effective in the DMSO-water mixture.

Using poly(2-vinylpyridine) or poly(4-vinylpyridine) with poly(monomethyl itaconates), Katime et al. [72] synthesized two different types of materials depending on solvent. In both systems, the experimental data obtained by Fourier-Transform Infrared (FTIR) spectroscopy confirmed hydrogen bonding between poly(vinylpyridines) and poly(monomethyl itaconates). When methanolic solutions of polymers were mixed, a white gel-like precipitate was observed. The composition of the solid was determined by the condition of mixing. The process was independent of the initial concentration of the solutions and the temperature. On the contrary, both polymers remained in solution if pyridine was used as a common solvent. Pyridine inhibited polymer-polymer complex formation.

Temperature dependence of intrinsic viscosity of poly(methacrylic acid)-poly(vinylpyrolidone) system in water and DMSO and also of poly(methacrylic acid) in DMSO at 25-100°C was investigated by Bekturov et al. [73]. They showed that complex structure was stable in water and was not destroyed by the thermal action, intrinsic viscosity did not depend on temperature. The destruction of complex in DMSO caused a significant increase of the poly(vinylpyrolidone)-poly(methyacrylic acid) system's viscosity which did not change with increase of temperature.

According to Bekturov [16] polymer complexes formed in aqueous solutions are more stable than complexes obtained from organic solvents. Mun et al. [68] also explained that polymer complexes formed in aqueous solutions were more stable than complexes obtained from organic solutions. In organic solutions, the acid-base equilibrium shifted to unionized carboxylic groups that favor H-bonding complex formation. They studied the complex formation between poly(acrylic acid) and poly(vinylether) of ethylene glycol in ethanol and isopropyl alcohol by turbidimetry. They showed the destruction of the complex by addition of N,N-dimethyl formamide (DMF).

In dilute aqueous solution, Staikos et al. [74] presented potentiometric and viscometric results on the interpolymer complexation between poly(acrylic acid) and poly(acrylamide). The temperature dependence of the strength of the formed complexes was investigated. From the results obtained, they concluded that hydrogen bonding was the main factor stabilizing the complex, and strengthened by decreasing the temperature.

An attempt was made by Ferguson et al. [39] to gain better understanding of the complexation between poly(acrylic acid) and poly(vinylpyrolidone), and the influence of the presence of Cu^{2+} ions in aqueous and ethanol-aqueous solutions. Interpolymer complex formation between two polymers was mainly due to hydrogen bonding. It was found that the rate of complexation was enhanced in the presence of Cu^{2+} ions, also it was more pronounced in water than in an ethanol-water solution.

2.6. Physical and Chemical Properties of Interpolymer Complexes

Interpolymer complexes usually show a physical behaviour quite different from that of the pure components. They have the following properties;

1) Physico-chemical properties (insolubility in water, highly specific but limited water absorption)

2) Selectivity of ion sorption and ion exchange properties

3) Transport properties (high permeability to water, electrolytes, inpermeability to macro-solutes)

4) Heat stability.

Inter polyelectrolyte complexes composed of a strong polyacid and strong polybase are insoluble in common organic and inorganic solvents. They are only soluble in specific ternary solvent mixtures [11]. Deng et al. synthesized polyelectrolyte complex using imidazolinium organosilicon copolymer with poly(sodium styrene sulfonate). PEC was dissolved in ternary system consisting of inorganic salt (NaCl, NaBr, NH_4SCN), organic solvent (DMF) and water at 30°C [75]. Oyama et al. [76] prepared stoichiometric and nonstoichiometric polyelectrolyte complex from poly(sodium styrene sulfonate) and poly(diallydimethyl ammonium chloride). Polyelectrolyte complexes were dissolved in a ternary solvent composed of water, dioxane and 37.7 % HCl, (3:3:4 by weight ratio). Dissolution was thought to occur because of the separation into the two individual polyanion and polycation components. The dried powders of stoichiometric and non-stoichiometric complexes

were dissolved in the ternary solvent. The solution of the polycomplex was cast on a glass and a transparent film was obtained.

Interpolymer complexes have extremely high and controllable permability to water and low molecular weight solutes. Oyama et al. Investigated the sorption properties of complex that was formed from poly(acrylic acid) and poly(4-vinlypyridine) [77]. One gram of polymer samples and complex were kept for one month under a certain pressure at 313 K for conditioning; They were then dried in vacuum oven at 333 K and set in desiccators where different saturated salt solutions kept the vapor pressure constant. It was found that the sorption of water vapor by an equimolar complex at 293 and 303 K was higher than that by the pure components. At low pressures, the sorption properties was effected by the composition of the complex.

The water sorption behaviour of the interpolymer complex [poly(4-N-methacrylamid benzoic acid)–chitosan] was analysed by Peniche et al. [78].

Huglin et al. [33] reported that the glass transitions of complexes formed between poly(4-vinylpyridinium chloride) (P4VPHCl) and poly[sodium(2-acrylamido 2-methyl propanesulfonate)] (PAMPSNa) could not be detected, due to the very high ionic crosslinking density. A similar problem in detecting Tg's has also been encountered in complexes formed between poly(monomethyl itaconate) with P4VP [79].

Avramenko et al. [80] discovered three component interpolymer complexes from two polymers [poly(acrylic acid) and poly(sodium phosphate)] and low molar mass bases such as 4-vinylpyridine and 2-methyl-5-vinylpyridine DSC curves of three component interpolymer complex was different from the model mixtures formed by each polyacid with the low molar mass base. The complex was not a mixture of three components, but was a individual compound.

There are some studies of reactions in a ternary system of macromolecules. Such reactions are of particular interest to an understanding of the processes which take place in biological systems where natural polyelectrolytes are present. Izumrudov et al. [81] investigated the substitution reactions on a macromolecular system containing two different types of polyanions, namely sodium polymethacrylate (Na-PMAA), sodium polyethylene sulphonate (NaPES) and the polycations of poly(4-

vinylpyridinium bromide) (P4VEBr). The substitution was carried out by adding to the solution of the PEC (PMAA-P4VE) portions of the competing polymer NaPES.

If P_1(polymer 1) can react with P_2(polymer 2) more strongly then P_3(polymer 3), the interchain macromolecular exchange reaction of P_3 and P_1 takes place on the addition of P_1 to P_2-P_3 complex solution.

$$(P_2\text{-}P_3)_{complex} + P_1 \rightarrow (P_1\text{-}P_2)_{complex} + P_3 \qquad (2.1)$$

Such exchange reactions may proceed by the following mechanism;

$$(P_2\text{-}P_3)_{complex} + P_1 \rightarrow (P_1\text{-}P_2\text{-}P_3)_{complex} \rightarrow (P_1\text{-}P_2)_{complex} + P_3 \qquad (2.2)$$

Before the complex (P_2-P_3) is completely destroyed, the third polymer (P_1) component interacts with the first complex to form a ternary complex (P_1-P_2-P_3). Then , the first polymer component (P_3) is dissociated from the ternary complex [82, 83].

Interpolyelectrolyte substitution reactions of fluorescence-tagged poly(methyacrylate) polyanions and poly(phosphate) anions with different poly(N-alkyl-4-vinylpyridinium) polycation was studied in the region 278-333 K using fluorescence method by Izumrudov et al. [84]. The possibility of effective temperature control of the interpolyelectrolyte reaction might be important for understanding, prediction and utilization of transformation process of complex particles formed by electrostatically biological macromolecules.

2.7. Applications of Interpolymer Complexes

In spite of the short period of intensive investigation of polyelectrolyte complexes, their outstanding physico-mechanical, ion-exchanging and optical properties have roused a great interest in the polymer materials. The first systematic studies on the properties of polyelectrolyte complexes were carried out by Michaels et al. [1, 11]. They examined the complexes of strong, oppositely charged polyelectrolytes. It was shown that the polyelectrolyte complexes have original physico-chemical properties

such as insolubility in common solvents; ability to plasticize in water and electrolyte solutions, high absorption of water, alcohols, etc. and sorption, ion-exchange selectivity. Polyelectrolyte complexes are highly permable to water, gases, dissolved low molecular weight substances and not permeable to macroscopic particles. There exists a number of practical applications of polymer complexes. However, few publications are found in the open literature.

Polyelectrolyte complexes are very promising materials for preparing semi-permeable membranes [85]. The membranes are formed either by preparing the complex as a gel or by preparing a mixture of the components in a suitable solvent medium and transformation of this solution to a complex membrane. These membranes are applied for the desalting of sea water, for ultrafiltration in purifications and concentration of water solutions containing micro and macroparticles [86]. These membranes are also used for the ultrafiltration of biological liquids [87].

Polyelectrolyte complexes can be used for microencapsulation of biological materials. The principle of encapsulation was developed by Dautzenberg et al. [2].

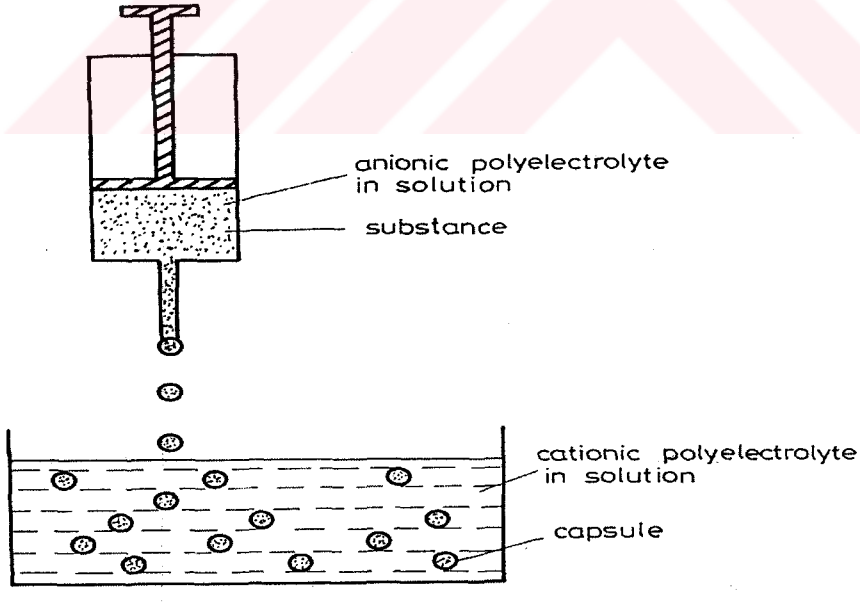


Figure 2.4. Microcapsule preparation.

The sample to be encapsulated is suspended or dissolved in the solution of the anionic polyelectrolyte. The droplets of the system are then reacted in a precipitation both with a suitable cationic polyelectrolyte to form a complex microcapsule with a liquid core containing the material to be encapsulated. Enzymes, cell fragments were succesfully immobilized by this method without losing their biological activity [88, 89]. Polyelectrolyte complex formation can be used as a process to eliminate harmful or unwanted products from biological system. Concentration of harmful substances like lipids can reduce by coprecipitation with complex particles. Some serum proteins in human serum have been isolated by complexation with water soluble non ionic polymers.

The potential applications of hydrogels from polyelectrolyte complexes to contact lenses has been shown by Refojo [90]. He investigated the complexes of poly(vinyl benzyl trimethyl ammonium) and poly(styrene sulfonate). They were transparent, water insoluble materials. The permability of water of a series of polyelectrolyte complexes was determined.

Polyelectrolyte complexes as films or fiber materials may be used as separators ingalvanic and storage batteries [91]. These separators are stable in concentrated acids (sulfuric and phosphoric acid) and alkalies at moderate temperatures.

Films made of polyelectrolyte complexes exhibit high electroconductivity which does not change much with temperature and humidity. These films are used for preparation of transparent and electroconductive plates for heating purposes.

2.8. Poly(vinypyridines)

The poly(vinylpyridine) homopolymers, poly(4-vinyl pyridine) and poly(2-vinypyridine) resemble polystyrene. However, the presence of the nitrogen atom imparts basic properties to the polymer and alters its physical and chemical properties [92].

2.8.1. Properties of Poly(vinylpyridines)

a) Thermal Properties

Thoroughly dried poly(4-vinylpyridine) has well defined glass transition temperature of 140°C [31,72] and it is thermally stable up to 300-350°C under nitrogen atmosphere. Although the decomposition temperature for poly(2-vinylpyridine) has not well determined, the polymer is stable up to 200°C. The thermal stability of the polymers decreases upon conversion to an acid salt. Thermal stability decreases with the extent of quaternization.

b) Adhesion

Little discussion of the adhesive properties of the poly(vinylpyridines) has appeared in the literature, but it has been observed that the polyvinylpyridines can be made to adhere to glass, ceramic materials, most metals and a variety of plastics.

c) Solubility

The poly(vinylpyridines) are soluble in some organic solvents and aqueous mineral acids, but are insoluble in water. Good solvents include methanol, ethanol, dimethylformamide, pyridine. Non solvents include cyclohexane, heptane and toluene. The vinylpyridine homopolymers are moderately hygroscopic. The polymers (free bases and quaternary salts) can be dried in a laboratory oven at temperatures ranging 65-100°C.

d) Basicity

The apparent pKa's of poly(2-vinylpyridine) and poly(4-vinylpyridine) at half neutralization determined are at 20°C are 4.4 and 4.2, respectively [35].

e) Electrical Properties

The poly(vinylpyridines) in dry and relatively pure form exhibit insulating properties typical of most polymers. However, quaternization with alkyl halides or addition of acids to the free base can impart semiconducting properties to the polymers. Interest has recently been focused on highly conductive polymers such as polypyrole-BF_3 or poly(phenylene). These polymers are expensive and have mechanical properties

which make them difficult to process. In contrast, many poly(vinylpyridine) complexes, acid salts, quaternary alkyl halide salts which exhibit semiconducting properties are relatively easy to process. They are also commercially available at a lower cost than other conducting polymers.

2.9. Poly(phosphates)

Linear metal and ammonium polyphosphates of high molecular weight can be prepared by thermal dehydration of the corresponding metal or ammonium dihydrogen phosphate:

$$nMH_2PO_4 \rightarrow (MPO_3)_n + nH_2O$$

The type of polymer formed, its molecular weight, crystallinity and other properties depend not only upon the nature of the cations present, but also upon the conditions used for the dehydration.

2.9.1. Poly(sodium phosphate)

Poly(sodium phosphate) are interesting from the scientific view point because they are totally inorganic polyelectrolytes and easily prepared to a degree of purity much higher than is commonly attained with organic polymers [93]. From the biological viewpoint polyphosphates are somewhat analogous to the nucleic acids.

Polyphosphates are widely employed in many fields [94, 95];

a) Food Applications:

A number of different chain phosphates have been employed to a considerable extent in the manufacture of sasuage products. The addition of poly(sodium phosphate) to sausage products in the range of 0.1-0.5% leads to a reduction in shrinkage of the product during boiling.

b) Metal Surface Cleaning Applications

Metal surfaces are washed with a greater variety of compositions than more porous surfaces. More work has been done on metal cleaning than other materials, because metals must be cleaned during manufacture as well as their finished form. Polyphosphates have been utilized in some patented cleaning compositions.

c) Water Treatment Applications

The treatment of water covers both precipitation and cation-complexing procedures based on polyphosphates. Succesful removal of calcium and magnesium ions by precipitation, so-called chemical softening, was the first method used to soften water. All of the polyphosphate anions are strong complexing agents that tie up the cations, such as Ca^{2+} and Mg^{2+}, so that the usual precipitates cannot form. Poly(sodium phosphate) have been used in large amounts for water softening.

d) Fertilizer Applications

Polyphosphates are used as micronutrient carriers in agriculture. Essential trace elements are incorporated in the polyphosphate, which can be blended with a macronutrient fertilizer or added directly to the soil.

e) Biopolymers Applications

Polyphosphate salts are useful as cation-exchange resins in protein chromatography and peptide separations. Some polyphosphates are useful in frozen foods and stability of ice-cream and other products can be improved.

The polyphosphates are consired instable in aqueous solution and the solution is maintained under sterile conditions [96, 97]. According to calculations by Van Wazer [98] at pH 7.10 and at 5°C long chain phosphates hydrolyse 5 % in about a century, a year at 35°C.

2.10. Irradiation Effect on Polymers

During the high irradiation of polymers, the main effect produced is either degradation of the molecular chains or intermolecular crosslinking. As discovered by Dole in 1948 [99], one of the most important effects of radiation on polymers is the formation of crosslinks between the long-chain molecules [100]. A moderate number of crosslinks can often improve the physical properties of polymers so that the irradiated materials enhanced industrial performance. However, at very high crosslink densities, the materials, can become stiff and brittle. Conversely, the irradiation can break bonds leading to scission of the macromolecules. Scission processes usually produce deleterious effects, resulting in materials which are weak and soft. In many cases, crosslinking and scission proceed simultaneously. However, dependent on the molecular structure or the other properties usually predominates.

Figure 2.5. Illustration of two radiation induced processes, scission and crosslinking (From Ref. [113]).

Many other radiation effects can occur, including the formation of double bonds and the elimination of gaseous products. When irradiation is carried out in the presence of oxygen, additional chemical reactions occur. The predominant reaction eventually determines the physical properties of polymers.

2.10.1. Factors Effect Radiation Resistance of Polymers

Radiation resistance is becoming an increasingly important consideration in design of much equipment for nuclear instrumentation and for aerospace and military purposes. Therefore, the effect of radiation on mechanical properties of polymers is of practical importance. Comparison of mechanical properties of polysulfones that

irradiated at various temperatures in air-vacuum environments was done by Brown et al. [101].

Polymers composed of only aromatic units are expected to be the materials used in fields such as in space and fusion reactor environments. To be able to use materials in such fields, knowledge of their radiation damage and/or resistance is required. In literature, radiation effects on polymers with various chemical structures have been studied.

Lawton et al. [102] determined the importance of physical state (crystalline, amorphous, or glassy) during irradiation. They found that crosslinking produced during irradiation was mainly in the amorphous areas of the polymer. Radicals were trapped in the crystalline regions and they could react with oxygen to form carbonyl groups, rather than crosslinks.

A direct method had been developed for determination of the radiation effect on chemical yields of crosslinking G (crosslinks), and scission G(s) for the irradiated polymers, polystyrene using analytical centrifuge method by Kells et al. [103].

Nichol et al. [104] observed that irradiation of polystyrene in air decreased the efficiency of crosslinking and enhanced that of scission.

The effect of gamma irradiation on polystyrene had been investigated by O'Donnel et al. [105]. By comparison with previous experimental results for polystyrene irradiated in air it had been established that an oxygen environment leaded to enhanced scission at the expense of crosslinking.

Crosslinking and chain scission both occured when polysulfones were subjected to γ-irradiation [106,107]. Insoluble gel was formed at high doses and the limiting viscosity number rised with increased dose when irradiation was carried out in vacuum. Irradiation in air resulted in no gel formation and decreased in limiting viscosity indicated that scission predominated over crosslinking.

Graessly [108] chosed polystyrene for the study because of easy preparation and charactarization as a linear polymer and also polystyrene was crosslinked by

radiation with few side reactions. Films of the polymers were crosslinked by γ-radiation and gel fraction as a function of radiation dose was determined.

Parkinson et al. [109] compared the measurements of crosslinking in polystyrene irradiated with γ-irradiation and with γ-neutron field.

Irradiation effects of ten kinds of polymers containing various aromatic rings linked by functional groups in the main chain were studied by Sasuga et al. [110]. The polymers studied were polyimides, polyetherimide, polyamides, poly(ether-ether ketone) (PEEK), polyarylate, polysulfones, poly(phenylene oxide). Based on the experimental results, the following order was proposed as for the radiation stability of the polymers; Polyimide > PEEK > polyamide > polyetherimide > polyarylate > polysulfone , poly(phenylene oxide).

The effects of varying gamma irradiation doses and dose rates on the radiation hardness of two polymers, poly(styrene) and poly(isobutyl methacrylate) were examined by Taylor and Harmon [111]. They found that at a constant dose rate, poly(styrene) showed increased transmission loss with increased doses up to 7 Mrads while poly(iso butyl methacrylate) showed increasing transmission loss up to 4 Mrads.

Mateev et al. [112] investigated the macromolecular structure and crosslinking parameters of polyethylene films after irradiation.

Results are summarized as follows;

1) Radiation resistance depends strongly upon chemical structure.

2) Radiation resistance is markedly affected by the irradiation conditions,for instance, temperature, crystallinity, molecular weight, the presence or absence of oxygen during irradiation [113].

In the absence of oxygen, irradiation produces a net crosslinking effect which occurs preferentially in the amorphous phase [114]. Irradiation of polymers in air decreases the efficiency of crosslinking and enhances that of scission. Some of the polymeric radicals that would normally contribute to crosslinking are believed to react with oxygen to form peroxides, which than decompose and cause oxidative degradation of

the main polymer chain [104, 115]. The formation of carbonyl and hydroxyl groups, initiating chain scissions diminish the physical and chemical properties of the polymers.

The temperature of the sample at the time of its exposure to irradiation is important. O'Donnell et al. [116] investigated the effect of irradiation temperature on crosslinking and scission for polystyrene. Polystyrene was subjected to γ-irradiation at 100 and 150°C. The yield of scission, G(scission), and crosslinking G(crosslinking) determined using gel permeation chromatography with supporting evidence from viscometry. The ratio of G(scission)/G(crosslinking) increased from 0.02 at 100°C to 2.8 at 150°C. This was mainly due to a tenfold increase in G(scission), whereas G(crosslinking) apparently decreased slightly.

2.10.2. Advantages of the Radiation Technique

Crosslinking can be produced by purely chemical means and radiation has considerable advantages and sometimes these cannot be readily achieved by other ways. Advantages of the radiation technique are [117-119];

1) The very extensive range of concentrations available

2) The absence of any chemical catalysts and residues. (Except those such H_2, CH_4, etc. which may be produced by the reaction, and are usually in the form of harmless gases).

3) The wide range of temperatures at which the reactions can be induced, with little dependence on temperature or irradiation.

4) Differential effect can be induced over a single specimen.

The introduction of random crosslinks between the chains in a solid polymer alters its solubility properties to the extend that, beyond a minimum crosslinking, a network is formed, and a uniform solution is no longer formed when the polymer is placed in a suitable solvent. With increasing crosslinking, the amount of the gel phase increases at the expense of sol, and the relative proportion of gel (the insoluble fraction) can be determined by extraction [108]. Estimation of the extent of reaction has also been made by measurement of solution viscosity, swelling ratio etc. [103].

CHAPTER 3 . OBJECTIVE OF THIS WORK AND SELECTION OF POLYMERS

Polyelectrolytes interact with various low and high molecular weight substances and form complexes [6,13,120,121]. The polymer complexes are usually obtained by mixing of pre-existing complementary components in the solution or by the matrix polymerization. There are some main factors affecting the formation of polymer complexes such as ionic strength and pH of the medium, temperature, polymer concentration, order of mixing of polyelectrolytes etc.

3.1. Poly(sodium phosphate) and Poly(4-vinylpyridinium hydrochloride) Interaction

Although numerous studies have been reported on the polyelectrolyte complexes, they emphasize on the polyelectrolytes of strong acids and bases. Very little is known about the interaction of polyelectrolytes which have relatively weak acids and base functions. Relatively polyelectrolytes of weak acid and base are of particular interests in this work since natural polyelectrolytes that play vital role in the biological systems are in general, weak electrolytes. The polymers selected for this study are poly(4-vinylpyridinium chloride) (P4VPHCI) and poly(sodium phosphate) (PSP). PSP is interesting because it is an inorganic polymer and is, rather unusually one of the few anionic polymers of the integral type, and is soluble in water. Polyphosphates are somewhat analogous to the nucleic acids. They are easily prepared and they are widely employed in many fields, beginning with mineral fertilizers and ending with medicinal and cosmetic preparations. They also strongly bind polyvalent cations.

It is apparent from literature (pages 8-16) that the main aspects studied by different authors are the composition of PEC obtained under various experimental conditions

and stoichiometry of polyelectrolyte complex reactions by different techniques. The schemes of the study related to the polyelectrolyte complex obtained by PSP and P4VPHCI are;

1) Stoichiometry of polyelectrolyte complex and factors affect stoichiometry (order of addition, ionic strength, and pH of the medium).

2) Confirmation of stoichiometry by analysis of supernatant liquids in conjunction with the weights of initial components and complex.

3) Thermal properties of polyelectrolyte complex formed.

4) Obtaining a complex in dilute solution and demostration of its presence and its change of shape with time.

5) Breakdown and suppression of polyelectrolyte complex formed.

3.2. Poly(sodium phosphate) and 4-amino benzoic, hydrochloride Interaction

Studying the pecularities of polycomplex formation between polymers and low-molecular weight substances can be helpful in understanding the nature of protein-lipids interactions in biomembranes or the mechanism of protein denaturation etc. It is known that polyelectrolytes interact with various low and high molecular weight substances and form polyelectrolyte complexes which usually precipitate from aqueous solution [6,13].

Polyelectrolyte complex precipitates are obtained by mixing PSP and 4-aminobenzoic acid, hydrochloride (PABCI). The schemes of the study related to this complex are;

1) Stoichiometry of polyelectrolyte complex and confirmation of stoichiometry by analysis of supernatant liquids in conjunction with the weights of initial components and complex.

2) Obtaining a complex in dilute solution and demostration its presence using methods; viscometry, conductometry and potentiometry.

3) Temperature effect on viscosity's of each component and complex.

4) Dissolution of complex in different solvents and after dissolution potentiometric titration of complex in non-aqueous solution.

5) Interaction between polyelectrolyte complex and metal ion.

3.3. Poly(4-vinylpridine) and 4- amino benzoic acid Interaction

Poly(4-vinylpyridine) is such a polymer that is weakly self associate. The pKa value of P4VP is 4.2 at 298 K [35]. It contains a basic nitrogen that can form hydrogen bonds with carboxylic acid proton.

In this part of the study, the interaction between a small molecule, 4-aminobenzoic acid (PABA) and a synthetic polymer, poly(4-vinylpyridine) in non-aqueous solution is concerned.

Polymer complexes will be prepared in the laboratory by mutual precipitation or by casting films from solution. The schemes of the study related to P4VP and PABA interaction is;

1) Preparation of P4VP-PABA complex and characterization of polymer-small molecule complex using experimental techniques.

2) Dissolution of P4VP-PABA complex and determination of protonation constants of it using potentiometric method after dissolution.

3) Titrations of Cu(II) ions with P4VP-PABA complex potentiometrically and calculations of formation constants of (P4VP-PABA)-Cu^{+2} complex..

3.4. Irradiation Effects on Poly(4-vinylpyridine)

Poly(vinylpyridines), in general, would be expected to combine high radiation resistance with their thermal properties because of their aromatic contents. Knowledge of the changes in thermal properties of the polymer on irradiation is

important for their applications in many fields such as advanced composites and as an insulating materials for wire and cables in nuclear power plants.

In the present study, P4VP is the precursor of polycation (P4VPHCl) used for PEC formation. For having the progressed swelling properties of PEC, irradiation effect on P4VP was investigated.

In literature, there are lots of studies about the effects of irradiation on polystyrene. Although the vinyl pyridine monomers are similar to styrene except the presence of nitrogen atom on the pyridyl ring, there is not any study about irradiation effects on poly(vinylpyridines). The schemes of the study related to irradiated poly (vinylpyridines) are;

1) The role of chemical structure in radiation effects.

2) Dependence of the gel fractions of samples on irradiation dose.

3) It is known that when polymers are subjected to radiation, two kinds of reaction can occur. These reactions are crosslinking and chain scission. In this study, the efficiency question is to find the intensity of crosslinking and destruction processes and to define which process is to what degree.

4) If possible, preparation of gels and characterization with respect to their swelling properties.

5) Quaternization of irradiated P4VP sample and investigation of reaction between quaternized gel in poly(sodium phosphate) solution.

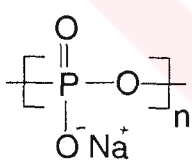
CHAPTER 4. EXPERIMENTAL PART

4.1. Materials

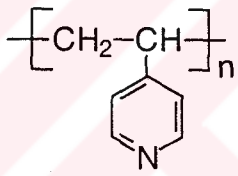
Poly(4-vinylpyridine) (P4VP) was obtained from Reilly Industries Inc. as a 25 % (w/w) solution in methanol.

Poly(sodium phosphate) (PSP) was supplied from Aldrich Chem. Co.

PSP and P4VP have the following molecular structures;



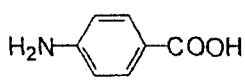
PSP



P4VP

(4.1)

4-amino benzoic acid (PABA) ($C_7H_7NO_2$) was a product of Merck. Its molecular weight was 137.14. It has a melting point of 186-188°C and it has the following molecular structure;



(4.2)

PABA

Ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) has a molecular weight of 1235.86 was supplied from Carlo Erba and used as a reagent for phosphate analysis.

Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$) is a commercial product of Merck with a molecular weight of 140.46. It was used as an electrolyte for potentiometric titrations.

N,N-dimethylformamide (DMF), (C_3H_7NO) and dimethyl sulfoxide (DMSO), (C_2H_6SO) were the products of Fluka. They were used as solvents for potentiometric titrations.

Tetrabutylammonium hydroxide (TBuAH), ($C_{16}H_{37}NO$) 0.1 M standard solution in 2-propanol/methanol was purchased from Fluka for potentiometric titrations in non-aqueous medium.

Ethanol (absolute) (C_2H_5OH) was the product of Carlo Erba.

Hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sodium hydroxide (NaOH), sodium bromide (NaBr), sodium chloride (NaCl) were all reagent grade quality (Merck).

4.2. Equipment

Conductometer

Conductometric titrations were performed using an ATI Orion Model 162 conductometer at constant temperature in a thermostated water bath.

pH Meter

Potentiometric titrations were carried out with a Jenway 3040 ion analyser at constant temperature.

UV Spectrophotometer

Hewlett-Packard 8452 and Shimadzu UV-160 A spectrophotometers were used for measurements.

Differential Scanning Calorimeter

Differential scanning calorimetry (DSC) measurements were made with Mettler TA-3000 and Perkin-Elmer DSC 6 instruments . The glass transition temperatures were determined using a heating rate of 10°C min^{-1}.

Fourier Transform Infrared Spectrophotometer (FTIR)

Infrared spectra of polymers and complexes were obtained using a Mattson 1000 FTIR Spectrophotometer at room temperature.

Viscometer

The measurements were performed in a Ubbelohde capillary viscometer (Model AVS 440, from Schott-Grade) in a thermostatically controlled bath at 29870.1 K.

4.3. Experimental Methods

Unquaternized P4VP that obtained as a 25 % (w/w) solution in methanol from which the solid was obtained by evaporation of solvent. The measured value of the limiting viscosity number in ethanol at 298 K (19.3 mlg^{-1}), in conjuction with the Mark-Houwink constant [122],

$$[\eta] = 25x\ 10^{-3}\ M^{0.68} \qquad (4.3)$$

yielded a molecular weight of $17.6x10^3$ $gmol^{-1}$. Conversion of the polysalt, poly(4-vinylpyridiniumchloride), P4VPHCl was obtained by the addition of the stoichiometric quantity of standardised aq. HCl followed by evaporation and final drying in a vacuum oven at 314 K. The degree of quaternization of 97 % was yielded a gravimetric method, and by a volumetric procedure [123].

The measured value of the limiting viscosity number of PSP in 0.415 M aq. NaBr at 298 K (2.6 mlg^{-1}) , in conjuction with Mark-Houwink constants [124],

$$[\eta] = 49.4\ x\ 10^{-3}\ M^{0.50} \qquad (4.4)$$

gave a molecular weight of $2.77x10^3$ g mol^{-1}. The GPC analysis in 0.5 M aq $NaNO_3$ based on poly(ethylene glycol) calibration afforded $M_w=2.10x10^3$ $gmol^{-1}$ and $M_w/M_n=1.14$ (M_w=Weight average molecular weight, M_n=Number average molecular weight. It involves a count of the number of molecules of each species

divided by the total number of molecules). Measurements on solutions of P4VPHCl under similar conditions proved unsatisfactory result probably due to the cationic nature of the polymer and the column characteristics.

The number average degree of polymerization of PSP was also obtained by end group analysis [125]. Orthophosphate is the monomer of polyphosphates. The chain phosphates have one strongly ionised hydrogen for each phosphorus atom and have one weakly ionised hydrogen at each end of the chain. By titrating this weak hydrogen it is possible to determine the number of end groups present in the chains.

A sample of PSP was dissolved in water and the pH was lowered to ca.3 with HCl in order to convert polyphosphate to phosphoric acid. Potentiometric titrations vs. aq. NaOH was conducted through the first (ca.pH 4.5) and second (ca. pH 9) end points between which the number of moles of base consumed (A) corresponds to the weak hydrogen of polyphosphoric acid.

To determine the total phosphorus content, polyphosphate was degraded by hydrolysis to orthophosphate (monomer of polyphosphate) by boiling the solution containing a known mass of sample, in 1 M HNO_3 for 2h. The pH was lowered to ca.3 with HCl in order to convert orthophosphate to orthophosphoric acid. Potentiometric titration vs. NaOH was then conducted through end points near pH 4.5 and 9. Because, there is one strong hydrogen ($K_{a1} = 10^{-3}$) for each phosphorus atom.In the case of chain compound, there is also a weak hydrogen ($K_{a2} = 10^{-9}$) at either end of the chain. The combination of the strong and weak hydrogens results in the inflection points in the titration curves at pH values near 4.5 and 9. In addition, there is an extremely weak third hydrogen on orthophosphoric acid ($K_{a3} = 10^{-13}$), a hydrogen which is too weak to titrate. Pure chain acids exhibit about the same pH as that of orthophosphoric acid. However, if the one hydrogen per phosphorus atom is partially neutralized, the longer chain acids are found to act as if they were weaker as neutralization proceeds, with the apparent strength of the acid at a given amount of partial neutralization increasing for shorter chain lengths. The number of moles of base consumed (A_h) corresponds to the total phosphorus in the sample.

$$\text{Fraction of total } P_2O_5 \text{ as end groups} = \frac{A}{A_h} \qquad (4.5)$$

As every chain is limited by two end groups, it follows that in a sample containing only chain phosphates, the number average chain length ($\overline{X}_n$) of the phosphate is given by;

$$P_2O_{5\,(total)} / P_2O_{5\,(end)} = \overline{X}_n / 2 \qquad (4.6)$$

4-amino benzoic acid, hydrochloride (PABCl) was obtained by addition of stoichiometric amount of standardised aqueous HCl solution into 4-amino benzoic acid (PABA).

4.4. Interaction Between Poly(sodium phosphate) and Poly(4-vinylpyridinium chloride)

4.4.1. Formation and Separation of PEC

Two series of PEC were prepared by mixing 0.2 M PSP and P4VPHCl solutions, where molarity M is in moles of monomer units per liter. The mole fractions of $4VPH^+$ units in the feed (X_{4VPH^+}) were 0.1, 0.3, 0.5, 0.7, 0.9 (The mole fractions of PO_3^- units were 0.9, 0.7, 0.5, 0.3, 0.1). In series 1; P4VPHCl was added dropwise to PSP, in series 2; the order of addition was reversed. Before mixing, the individual solutions were clear, but upon mixing, precipitates formed immediately. After isolation of precipitates by centrifugation, they were washed repeatedly with distilled water and dried to a constant mass in vacuo at 343 K (Table 5.1).

4.4.2. UV Analysis of Supernatant Liquids

The supernatant liquids associated with each PEC from series 1 and series 2 were analysed by UV spectroscopy. P4VPHCl has an absorbance peak at 260 nm (λ_{max}=260 nm), at which wavelength PSP does not absorb. The absorbance of standard solutions of P4VPHCl, having concentrations between 10^{-4} and 10^{-6} M was measured at this wavelength and found to obey the Lambert-Beer law, the extinction coefficient having a derived value of 2681 $Lmol^{-1}cm^{-1}$ (Figure 4.1).

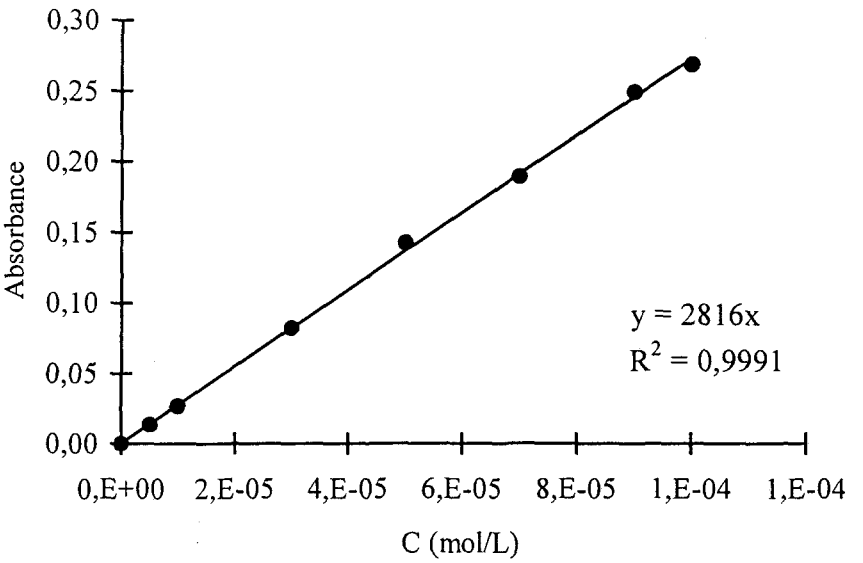


Figure 4. 1. The absorbances of standard P4VPHCl solutions at 260 nm.

Formation of a yellow precipitate on reaction of orthophosphate in polyphosphate with molybdate in acidic solution utilised to determine colorimetrically the phosphorus content of the supernatant liquid [126].

Monopotassium phosphate was used as standard reference material after driying at 378 K for 1h, and then 0.02 % by weight solution of monopotassium phosphate was prepared. A 3.76 % by weight solution of ammonium molybdate was prepared, by initial dissolution in water followed by an addition of concentrated H_2SO_4 and finally dilution to a fixed volume with distilled water. To 2 ml ammonium molybdate was added separately 1, 2, 3, 4, 5 and 6 ml of the monopotassium phosphate solution, 10 ml acetone and sufficient deionised water to yield a final volume of 25 ml. To determine the total phosphorus content, polyphosphate was degraded by hydrolysis to orthophosphate (monomer of polyphosphate) by boiling the solution containing a known mass of sample, in 1 M HNO_3 for 2h.

The absorbance of these standard solutions was measured at 338 nm using a blank that has been prepared from 2 ml ammonium molybdate solution, 10 ml acetone and final dilution to 25 ml with deionised water. Acetone was intensified the phosphomolybdate color and allowed complete solution of phosphates. The derived value of the extinction coefficient was 15.8 L cm^{-1} g^{-1} (Figure 4.2).

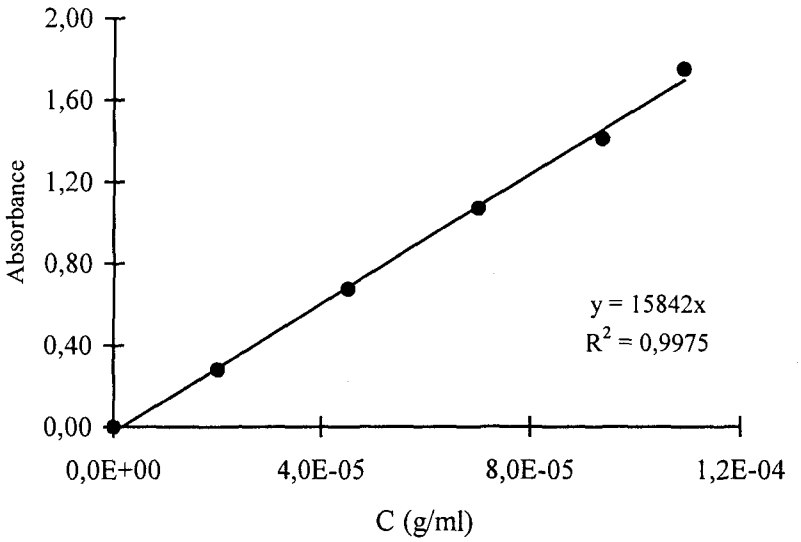


Figure 4.2. The absorbances of standard orthophosphate solutions in PSP at 338 nm.

After a centrifuge treatment the supernatant liquid and washings from each solution were collected and made up to a known volume with distilled water. Concentrations, and thereby, the total mass of unreacted P4VPHCl and orthophosphate in PSP in the supernatant liquids, were determined from the measured absorbances at 260 and 338 nm, respectively (Table 5.2). NaCl is produced in PEC formation. To examine its possible effect on the absorbance of the individual polyions, absorbance was measured on solutions containing a constant amount of polyion and different concentrations of NaCl.

4.4.3. Differential Scanning Calorimetry

Indium and zinc standards were used to calibrate the temperature and the thermal scale. The measurements to determine glass transition temperatures (T_g) of P4VP, P4VP-PABA and PSP-P4VPHCl complexes were carried out in a N_2 atmosphere at a heating rate of 10° C min^{-1} and the middle point criterion was used. In order to avoid differences in thermal history, all the samples were subjected to the same thermal treatment.

4.4.4. Optical Density

Measurements of optical density were used to investigate the situation prevailing in dilute (ca.$1x10^{-4}$ M) solution. The mixture of $1x10^{-4}$ M P4VPHCl and$1x10^{-4}$ M PSP

was stirred for at least 24 h and transferred to a 1 cm path length cell maintained at 29870.1 K. Optical density between 200 and 630 nm was scanned at 2 nm intervals. Scans were also made after additional periods of time [32].

4.4.5. Breakdown of PEC

To a fixed mass of dried PEC was added to a fixed volume of strong acid and a weak acid of various molarities and breakdown accompanied by dissolution after 48 h at room temperature was assessed visually. When dissolution did occur, the breakdown products were determined analytically. The breakdown products of PEC were identified by UV measurements. A part of the resultant solution was neutralised with NaOH, a precipitate obtained and isolated by centrifugation and dissolved in ethanol. Another part of the resultant solution, after removing the precipitate, was acidified and ammonium molybdate reagent was added, and an immediate yellow phosphate precipitate was obtained. The breakdown products after being identified qualitatively, their contents were analysed quantatively by UV measurements as detailed in Section 4.4.2.

4.4.6. Polyelectrolytes Complex in Dilute Solution

PEC formation in dilute solution was examined spectrophotometrically. Between 200 and 1000 nm PSP does not show any absorbance, whereas P4VPHCl has a maximum absorbance of 255 nm. While mixing dilute solutions of polyions, no precipitation was observed. None of the mixtures was turbid. To 1 ml of $1x10^{-3}$ M P4VPHCl were added separately 1, 2, 4 and 9 ml of $1x10^{-3}$ M PSP. Finally, all the solutions were diluted to 25 ml and the absorbances were measured.

4.4.7. Suppression of PEC Formation

To a fixed volume of standard aq. P4VPHCl were included various volumes of standard aq. NaCl (5 $molL^{-1}$) solution in order to assess visually whether the PEC precipitate produced or not by subsequent additon of standard PSP. The precipitation existed with the addition of NaCl solution less than 2.4 ml, a turbid solution is obtained at the 2.6 ml, and than over this limit volume, PEC was dissolved.

4.4.8. Turbidity Measurements

Turbidity of two series of PSP-P4VPHCl solutions were measured within the given range of wavelength and the curve of log τ vs. log λ was plotted. From the slope (β - 4) of linear curve β values were calculated for each measurements carried out for a period of 8 days (Table 5.4).

4.5. Interaction Between Poly(sodiumphosphate) and 4-amino benzoic acid, hydrochloride (PABCl)

4.5.1. Gravimetric Analysis of Polyelectrolyte Complexes

Two series of PEC were prepared by mixing 0.1 M PSP and 0.1 M PABCl solutions, which was obtained by addition of stoichiometric amount of standardized aqueous (0.1 M) HCl into 4-amino benzoic acid solution. Components were fixed in the following mole ratios; 0.8, 1.0, 1.2, 1.5, 2.0. In series 1, PSP was added dropwise to PABCl; in series 2, the order of the addition was reversed. Precipitates from each reaction were isolated via centrifugation, washed repeatedly with distilled water until all ions not associated with PEC were removed and finally dried to constant mass in vacuo at 323 K.

4.5.2. Analysis of Supernatant Liquids

The supernatant liquids associated with PEC from series 1 and series 2 were analysed by UV spectrometry with respect to PABCl. PABCl has an absorbance peak at 274 nm (λ_{max}=274 nm) at which wavelength PSP does not absorb. The absorbance of standard solutions of PABCl, having concentrations between 10^{-4} and 10^{-6} M was measured at this wavelength and found to obey Lambert-Beer law, the extinction coefficient having a derived value of 3589.8 L $mol^{-1}cm^{-1}$.

The supernatant liquid and washings from each solution were collected and made up to a known volume with distilled water. Each solution would contain the excess component plus NaCl which would be released from the precipitate upon complete reaction between PSP and PABCl. Concentrations of chloride ion in the supernatant

liquids were determined by argentometry [127] to calculate the percentage of bounded PABCl with PSP (Table 5.7).

4.5.3. Viscosity Measurements

The reaction between PSP and PABCl was checked by measuring the specific viscosity of supernatant mixtures. The viscosity of mixture solutions was measured. For each mixture, a control sample was made up to contain the ionic excess of the component plus the amount of NaCl which would be released from the precipitate upon complete interaction between PSP and PABCl. The viscosities of these solutions were measured for comparison with the mixture supernatant viscosities (Table 5.8).

4.5.4. Dilute Solution Interaction

4.5.4.1. UV Spectrometry

PEC formation in dilute solution was examined spectrophotometrically between 200 and 1000 nm. PSP does not show any absorbance, whereas PABCl has a maximum absorbance at 274 nm. When mixing dilute solutions of PSP and PABCl, no precipitation was observed. None of the mixtures was turbid. Stock solutions containing PABCl and PSP were prepared as follows: First, stock solutions of PSP, $1.0x10^{-3}$ M and PABCl, $1.0x10^{-3}$ M were prepared. To 1 ml of $1.0x10^{-3}$ M PABCl were added separately 0.8, 1.0, 1.2, 1.5, 2.0 ml of $1.0x10^{-3}$ M PSP. Finally, all solutions were diluted to 50 ml and the absorbances were measured (Figure 5.3).

4.5.4.2. Viscosity Measurements

The viscosity of the mixed solutions of PSP, $1.0x10^{-2}$ M with PABCl, $1.0x10^{-2}$ M at various mole ratios was determined (Figure 5.4). The temperature dependence of viscosity of PEC was also investigated for the molar ratio of 1:1.2 (PSP/PABCl) (Figure 5.5).

4.5.4.3. Conductometric Titrations

The reactions were carried out by slow dropwise addition of titrant to the solution with rapid stirring. The solutions were maintained at constant temperature in a thermostated water bath. $1.0x10^{-3}$ M PSP was titrated with 30 ml of $1.0x10^{-3}$ M PABCl in the presence and the absence of NaCl (Figure 5.6).

4.5.5. Breakdown of Polyelectrolyte Complexes

A fixed volume of N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, ethanol, water, NaCl-water was added to a certain mass of dried PEC. Breakdown of complexes accompanied by dissolution at room temperature was assessed visually.

4.5.6. Cu (II) Interaction with PSP-PABCl Complex in Nonaqueous Solution

For standardization of pH measurements in nonaqueous solvents, buffer solutions were prepared from 0.05 m CH_3COOH, 0.05 m CH_3COONa and 0.05 m NaCl in water-methanol mixture (50 % w/w) [128], so the influence of the solvent on the liquid-junction potential at the tip of the electrode was taken into consideration. After dissolution of fixed amount of dried PEC in DMSO, the solution was titrated with 0.1 M tetrabutylammonium hydroxide (TBuAH) solution (Figure 5.8). PEC and cupric ions mixture in nonaqueous solution was titrated with TBuAH potentiometrically in the presence of 0.01 M $NaClO_4$. Uncomplexed Cu (II) ion was determined by Atomic Absorption Spectrometry. Stock solutions of Cu (II) were made from Titrisol (Merck) and further dilution with distilled water was made to prepare reference solutions. 24 ml of Cu (II) solution (0.254 g/100 ml) and 0.5 g PEC was put in a polyethylene vessel and shaken for 8 h. The PEC loaded with analyte washed with bidistilled water and then filtered. Copper amount of the washing content was determined by Atomic Absorption Spectrometry (Figure 5.9).

4.6. Interaction Between Poly(4-vinylpyridine) (P4VP) and 4-amino benzoic acid (PABA)

4.6.1. Preparation of PEC

4-amino benzoic acid (PABA) and poly(4-vinylpyridine) (P4VP) were dissolved in absolute ethanol at a concentration of 0.2 M. PEC was prepared by mixing appropriate amounts of solutions. Before mixing, the individual solutions were clear but, upon mixing, a cloudy solution was obtained and the precipitate could not be isolated by centrifugation. PEC was prepared by the evaporation from ethanol solution followed by drying at vacuo at 323 K.

4.6.2. Characterization of Polycomplex

PABA-PABCl complex was characterised using methods of FTIR spectroscopy, DSC, NMR and potentiometry. Samples were prepared by dispersing the compounds in KBr and compressing the mixture to form discs for FTIR spectroscopy measurements. The measurements to determine T_g were carried out in a N_2 atmosphere. The solutions for the potentiometric titrations were prepared by pipetting 3 ml of 0.1 M $HClO_4$, 2.5 ml of 1 M $NaClO_4$, 12.5 ml of ethanol and 7 ml of water into the titration vessel. 0.0217 g PEC. Titration of $HClO_4$ alone was also carried out using 0.2 M NaOH as titrant (Figure 5.15).

4.6.3. Cu(II) Interaction with PABA-P4VP Complex in Aqueous Ethanol Solution

For determination of formation constants of PEC-Cu^{2+} complex, two series of 25 ml solutions have been prepared; one is containing 0.065 g of PEC, 2.5 ml of 1 M $NaClO_4$, 12.5 ml of ethanol, 1 ml of 0.01 M $CuSO_4$ and 9 ml of water, the other is containing 0.065 g PEC in 2.5 ml of 1 M $NaClO_4$, 12.5 ml of ethanol and 10 ml of water. Both solutions have been titrated potentiometrically with 0.0173 M NaOH solution. The potentiometric titration data was evaluated to calculate the formation constants of PEC-Cu (II) by using Calvin-Melchior method (Figure 5.16).

4.7. Irradiation Effects on Poly(4-vinylpridine)

In order to investigate the swelling properties of P4VPHCl-PSP system PSP and P4VP were subjected to irradiation to increase the cross-linked structure which provides high swelling capacity.

4.7.1. Irradiation

P4VP was dissolved in ethanol and then solvent cast in a perti dish to give thin films of P4VP. The films were then dried in vacou at 343 K before irradiation.

The glass ampoules which contained P4VP films were put on a vacuum rig and evacuated for 4 hours, after which they were sealed. The glass ampoules were irradiated at a 4.5 MeV Dynamitron electron accelerator at Isotron Plc. to six different doses (0.20, 0.61, 1.03, 1.43, 1.84, 2.19 MGy). There was no discernible increase in temperature during the process in which each of the sample received a target dose of 32.25 kGy per pass. The ampoules were at ambient temperature before entering the irradiation cell for each pass.

4.7.2. Gel Determination

Each irradiated sample was weighed into a soxhlet thimble ($w_{initial}$) and extracted with ethanol for 15 hours to determine the insoluble part in the sample (w_{gel}) gravimetrically. This procedure was also used for the unirradiated samples. After extraction, amount of polymer dissolved in ethanol (w_{sol}) was determined by UV spectrophotometry [129]. At the end of the experiments, the sum of $w_{gel} + w_{sol}$ was equal to $w_{initial}$. The absorbances of standard solution of P4VP were measured at 264 nm. The absorbances of series of standard solutions of P4VP were measured at this wavelength and found to obey the Lambert-Beer law. The extinction coefficients having derived value of 4728 $Lmol^{-1}cm^{-1}$. After extraction, the gel percent in the irradiated samples was calculated as follows;

$$\text{Gel } \% = (w_i / w_0)\ 100 \qquad (4.7)$$

Where w_o represents the weights of dry irradiated samples (before soxhlet extraction, that contains both sol and gel part) and w_i, represents the dry insoluble (gel) part (Figure 5.19).

4.7.3. Swelling Measurements

Clean, dried irradiated P4VP films of known weights, after removal of sol fractions, were immersed in ethanol at 20°C until equilibrium was reached (24 h). The films were removed and blotted quickly with absorbent paper to remove the liquid attached to the surface and weighed in a stoppered weighing bottle. The ethanol uptake percent was calculated as follows:

$$\text{Ethanol uptake } \% = \frac{(w_s - w_d)}{w_d} 100 \tag{4.8}$$

Where w_d and w_s represents the weights of dry and swollen irradiated samples, respectively.

For gels, swelling data from the gravimetric analysis were used to calculate the volume fraction. V_{2m}, and equilibrium degree of swelling, q_v, of polymer in a given gel sample swollen to equilibrium in ethanol [130, 131].

$$q_v = \left(1 + \frac{\rho(q_w - 1)}{d}\right) \tag{4.9}$$

where q_w is the ratio of the weights of the network in the swollen state and dry state, ρ and d are the densities of polymer and ethanol, respectively. The equilibrium degree of swelling, q_v, was defined as $q_v = 1/V_{2m}$. Using the values of $\rho = 0.95$ gml^{-1} and $d = 0.786$ gml^{-1}, q_v values were calculated (Table 5.12).

4.7.4. Quaternization of P4VP Film

P4VP film that was irradiated with a dose of 0.20 MGy was quaternized. Quaternization was carried out by immersing the known amount of the sample in 0.1

mol L^{-1} HCl for 24 hours and then washed with water. The quaternized gel, thus obtained, was dried in vacuo at 318 K and weighed (w_g). According to the reaction P4VP + HCl $\rightarrow$ P4VPHCl if complete quaternization is achieved, theoretically the value obtained should be 0.347. Quaternization percent of P4VP film was calculated as follows;

$$\text{Quaternization } \% = \left(\frac{w_g - w_0}{w_0} \right) \tag{4.10}$$

Where (w_g) and (w_0) represent the weights of the quaternized and irradiated sample, respectively. The quaternization percent was 109 %.

4.7.5. Interaction of PSP with P4VPHCl Gel

Known amount of quaternized P4VP film was immersed in water during 24 h in order to achieve equlibrium state. The weight fraction of the polymer in swollen network was determined by the formula $\beta = m_{dry} / m_{sw}$ where m_{dry} is the mass of the dry gel and m_{sw} is the mass of the swollen gel. The values β for the quaternized P4VPHCl gel was 8.47×10^{-3} . To study the interaction of PSP with P4VPHCl film was put in PSP solutions and thermostated at 298 K until equilibrium was reached for 24h, then samples was dried to constant weight. The swelling coefficients (K_s) of the samples were determined gravimetrically according to the following expression;

$$K_s = \frac{(m_s - m_d)}{m_d} \tag{4.11}$$

Where m_s and m_d are the mass of the swollen gel and dry samples, respectively.

The salt effect and pH for K_s values of the complex were determined (Figure 5.26).

CHAPTER 5. RESULTS AND DISCUSSION

5.1. Interaction Between Poly(sodium phosphate) and Poly(4-vinyl pyridinium hydrochloride)

5.1.1. End Groups in Poly(sodium phosphate)

In the potentiometric titrations the values of A and A_h were 0.047 mol and 0.54 mol, respectively. Hence via Equations. 4.5 and 4.6 the values of the fraction of total phosphorus present as an end group and the number of average chain are calculated to be 0.09 and 23, respectively. The corresponding molecular weight is thus $23x102=2.35x10^3$ $gmol^{-1}$, which is similar to the values obtained by viscosity and GPC measurements.

5.1.2. Mass and Composition of PEC

The precipitate compositions were calculated by assuming that complete stoichiometric reaction and total counter ion release occurred in the relatively higher polyion concentration (0.2 M) [33]. As an example, in the mixing of **x** moles of P4VPHCl and **y** moles of PSP (where **y** is greater than **x**), the precipitate would contain **x** moles of each polyion, polyphosphate and poly(4-vinylpyridinium), and the supernatant liquid would contain **(y-x)** moles of PSP (the excess polyion) and **x** moles of NaCl (the moles of counterions released in a 1:1 pairing of oppositely-charged functions), i.e.:

$$\mathbf{y}\ \text{PSP} + \mathbf{x}\ \text{P4VPHCl} \rightarrow \mathbf{x}\ \text{PEC} + \mathbf{x}\ \text{NaCl} + \mathbf{(y-x)}\ \text{PSP} \qquad (5.1)$$

Reaction stoichiometry may be described by comparing the actual weights of precipitates (w_a) with the weights calculated on a stoichiometry bases (w_c).

Table 5.1. Comparison of the actual weights of precipitates (w_a) with the weights calculated on a stoichiometric basis (w_c).

X_{4VPH^+} in feed	w_c (g)	w_a (g)	w_a/w_c
Series 1 PSP as titrant			
0.1	0.074	0.058 ±0.002	0.784±0.027
0.3	0.222	0.191 ±0.015	0.860±0.068
0.5	0.370	0.344 ±0.018	0.930±0.049
0.7	0.222	0.191±0.014	0.860±0.063
0.9	0.074	0.056±0.003	0.757±0.041
Series 2 P4VPHCl as titrant			
0.1	0.074	0.055±0.002	0.743±0.027
0.3	0.222	0.192±0.012	0.865±0.054
0.5	0.370	0.352±0.019	0.951±0.051
0.7	0.222	0.230±0.006	1.036±0.027
0.9	0.074	0.056±0.003	0.757±0.041

The error is given as coefficient of variation

In Table 5.1, where X_{4VPH^+} denotes the mole fraction of 4-vinyl pyridinium units in the feed, it is seen that

(a) Generally actual weights are somewhat smaller than the calculated ones.This difference can be explained in either case, firstly the degree of quaternization of P4VP was 97% (indicated in Section 4.3) so that unprotonated groups cannot participate in the complex formation. Secondly, the PSP is a polymer of low molecular weight, and via Equation 4.5 the experimentally determined content of the end groups is not significant (8.7 %), therefore the reaction involving the endgroup is less effective in building up a complex than the reaction involving a main chain active unit.

(b) The order of addition does not affect the actual weights.

5.1.3. Mass and Composition of Supernatant Liquids

PEC compositions calculated from UV analysis of supernatant liquids for series 1 and series 2 are presented in Table 5.2.

Tablo 5.2. PEC composition calculated from UV analysis of supernatant liquids (A=calculated from UV analysis; D=C-B; F=E-D; I=G/(G+H)).

X_{4VPH^+} in feed	**A** 10^4x moles of $4VPH^+$ in washing	**B** $4VPH^+$ in washing (g)	**C** Weight $4VPH^+$ in feed (g)	**D** Weight $4VPH^+$ in complex (g)	**E** w_a (g)	**F** Weight phosphate in complex (g)	**G** 10^4x moles of $4VPH^+$ in complex	**H** 10^4x moles of phosphate ion in complex	**I** X_{4VPH^+} in complex
Series 1, P4VPHCl as titrant									
0.1	0.55±0.03	0.006	0.042	0.036	0.055±0.020	0.019	3.39	2.41	0.584±0.026
0.3	1.27±0.01	0.013	0.127	0.114	0.192±0.012	0.078	10.74	9.87	0.521±0.038
0.5	2.89±0.02	0.031	0.212	0.181	0.352±0.019	0.171	17.06	21.65	0.441±0.027
0.7	15.31±0.01	0.162	0.297	0.135	0.230±0.016	0.095	12.71	12.03	0.514±0.042
0.9	33.51±0.01	0.356	0.387	0.031	0.057±0.003	0.026	2.92	3.29	0.470±0.030
Series 2, PSP as titrant									
0.1	0.43±0.01	0.005	0.042	0.037	0.057±0.002	0.020	3.49	2.53	0.579±0.024
0.3	1.09±0.01	0.012	0.127	0.115	0.191±0.015	0.076	10.83	9.62	0.530±0.049
0.5	2.92±0.02	0.031	0.212	0.181	0.344±0.018	0.161	17.05	20.38	0.456±0.027
0.7	17.91±0.01	0.190	0.297	0.107	0.191±0.014	0.084	10.08	10.63	0.487±0.041
0.9	33.61±0.02	0.357	0.387	0.030	0.056±0.003	0.026	2.83	3.29	0.462±0.029

Each PEC composition was obtained from the concentration of unreacted polyions detected in the supernatant. As indicated in Table 5.2, estimated experimental errors ranging from ±0.024 to ±0.049 for the different mole fractions of P4VPHCl in PEC. Table 5.2 shows that

(a) Composition of PEC is independent of the order of polyion addition.

(b) For all feed mixtures, reaction stoichiometry is considered in 1:1 reasonably. The ratio of polycation to polyanion is 1.04 in average. The slight departures from 1:1 stoichiometry are probably due to errors associated with experimental conditions.

5.1.4. Breakdown and Suppression of PEC Formation

To assess the stability of the PEC, various solutions were added to a fixed mass (0.0163 g) of dried PEC, as noted in Section 4.4.5. Results are summarised in Table 5.3.

Table 5.3. The effect of various acids on PEC ((+) indicates breakdown; (-) indicates no reaction).

	Analytical Concentration of Acids ($molL^{-1}$)				
Acids	10^{-12}	10^{-4}	10^{-3}	10^{-2}	5.40
HCl		-	-	+	
HNO_3		-	-	+	
CH_3COOH					+

As it is seen from the Table 5.3 that the breakdown of complex occured at the concentration of 10^{-2} $molL^{-1}$ for strong acids. In the case of a weak acid, CH_3COOH (K_a=1.85x10^{-5}), breakdown occured at a molarity of 5.40 of which provides hydrogen ion concentration of 10^{-2} $molL^{-1}$. Extremely dilute solution of a strong base also breakdown the complex. The results of the experiments given in section 4.4.2 and 4.4.5 were 41.0% and 55.3 % for phosphate and of $P4VPH^+$, respectively. These values are comparable favourably with the theoretical calculations which were 42.7 % and 57.3 %, respectively. Breakdown of a PEC, in general, requires a more complex solvent mixture (often ternary).

The added NaCl was expected to affect the system in either way; one is it should suppress the complex formation due to excess charges on polyions that causes the regular ionic-crosslink between monomeric units being interrupted, that is, active groups cannot come to mutual position, thus PEC formation may not be proceed readily. This phenomenon is called suppression. However, polyions rearrange themselves by coiling their chains to ensure the active groups to react easily. Naturally such rearrangement might cause the changes in PEC stoichiometry. Secondly, NaCl provides common ion effect on polycation which is weak in nature, thus it dissociates largely and the PEC dissolves. At this point the ratio between mole numbers of NaCl to mole numbers of ionic monomers is found to be 33.

5.1.5. Polyelectrolyte Complex in Dilute Solution

The effect of addition of PSP on UV spectrum of P4VPHCl under the dilute conditions at pH 4.8 described in Section 4.4.6 is shown in Figure 5.1 relating to (a) P4VPHCl and four mixtures (b)-(e). The values of X_{P4VPH^+} (mole fractions) are 1.0, 0.50, 0.34, 0.20 and 0.10 in (a)-(e), respectively.

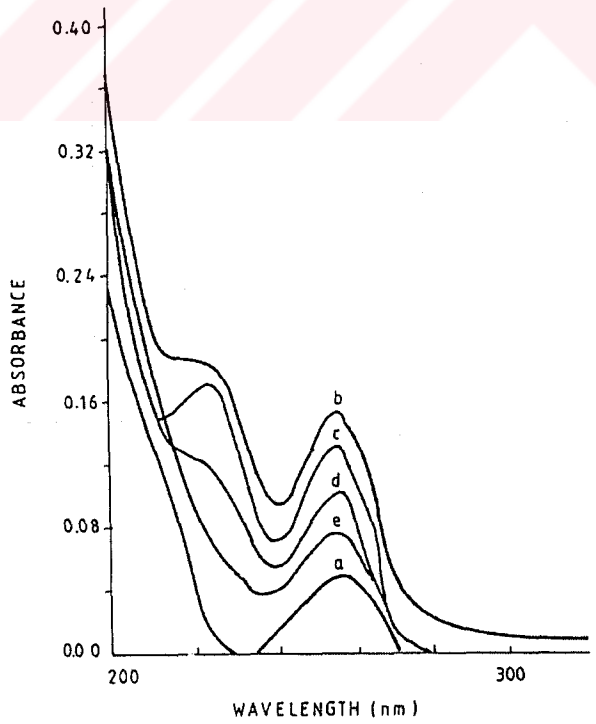


Figure 5.1. Effect of addition of PSP solution on absorbance of P4VPHCl. For explanation of (a)-(e) see text.

The PSP component does not have any absorbance between 200 and 1000 nm and the peak at 255 nm in all the curves is due to the pyridine ring. Although the mole fractions differ, the concentration of P4VPHCl was fixed at a constant value for all the systems. Hence, in the absence of any interaction between polyions, the absorbances at 255 nm would also be expected to remain constant. In fact for the complex mixtures, this absorbance is seen to increase with the increase in X_{P4VPH^+}. The values of $X_{PO_3^-}$ are 0.50, 0.66, 0.80, 0.90 in complex mixtures (b)-(e), respectively. Reaction conditions such as concentration of the components effect the formation of polyelectrolyte complexes. Increase in concentration of PSP enhances the contraction of the polymer chains. The amount of active sites in PSP was not sufficient to react with P4VPHCl so the absorbances of the mixtures decreases with increasing PSP concentration. In the complex mixtures an additional peak or shoulder appears at 220 nm, its absorbance following a similar sequence to that exhibited at 255 nm (at the lowest X_{P4VPH^+} the absorbance at 220 nm is only barely detectable). These shoulders are probably due to the formation of ionic bonds between the phosphate and pyridinium groups.

5.1.6. Turbidity

Measurements of turbidity, (τ) were carried out in order to get idea about the shape of polyions in dilute complex solution. For this study, the shape parameter β, should be evaluated firstly according to the following expression;

$$\tau \alpha \lambda^{\beta-4} \qquad (5.2)$$

As shown in Table 5.4, for the first series of sample solution (PSP as titrant) β values were ca. 1 for a period of 4 days thereafter they increased up to a value of ca. 2, whereas for the second series of sample (P4VPHCl as titrant) values were around 2 without depending on time. As it was indicated in reference [32] that when the polymer chains are rod like and spherical, β values are found to be 1 and 2, respectively.

Table 5.4. Calculated β values.

Time(days)	β	Time(days)	β
Series 1, PSP as titrant		*Series 2, P4VPHCl as titrant*	
1	0.96±0.08	1	2.31±0.02
2	0.98±0.02	2	2.24±0.01
3	1.12±0.01	3	1.93±0.03
4	1.14±0.03	4	1.82±0.05
5	1.61±0.04	5	a
6	1.73±0.02	6	a
7	2.02±0.01	7	a
8	2.03±0.05	8	a

[a] Due to the bacterial growth in polyanion β considered carrying uncertainities therefore they were excluded.

5.1.7. Glass Transition Temperatures

The DSC measurements on the solid PEC of different mole fraction displayed more or less the same T_g value. The results are shown in Table 5.5.

Table 5.5. Glass transition temperatures (K) of P4VPHCl-PSP complexes.

$X_{P4VPHCl}$ in feed	T_g	$X_{P4VPHCl}$ in complex
PSP as titrant		
0.1	401	0.57±0.02
0.3	425	0.53±0.05
0.5	414	0.46±0.03
0.7	394	0.49±0.04
0.9	392	0.46±0.03
P4VPHCl as titrant		
0.1	405	0.59±0.03
0.3	425	0.52±0.04
0.5	411	0.44±0.03
0.7	393	0.52±0.04
0.9	391	0.46±0.03

T_g values of P4VPHCl and PSP are 401 K and 540 K, respectively.

Results obtained are as follows,

(a) The order of addition in producing a complex has no effect on T_g, since the stoichiometry of complexes are about the same, T_g values would be expected to be same.

(b) However, the maximum experimental uncertainity is considered within ± 2 K, T_g values cannot be accepted as constant.

(c) The value of T_g, that can be calculated on the basis of the Fox equation for copolymers or blends, must lie in the interval 401-540 K. To this value should be added an increment due to the crosslinking. However, in the Table 5.5 it is seen that for two of the complexes the value of T_g is actually less than 401 K. The measured T_g value for the P4VP sample was 394 K and Eisenberg et al. [148] have obtained a value of 263 K for poly(phosphoric acid). On the basis of P4VP and assuming poly(phosphoric acid) as components of the PEC, the T_g should lie in the interval of 263-394 K with some additional increment for the crosslinking. In the case of salt form of polyionsT_g values of complexes should be lower than 263-394 K interval. However, the observed T_g values can be found to be higher than the expected values. The additional increment on T_g values of any of the PEC system might be in question due to the particular properties of the system. In this study, the components are in their salt form, therefore it is difficult to give a reasonable explanation for the high T_g values.

5.2. Interaction Between Poly(sodium phosphate) and 4-amino benzoic acid, hydrochloride

5.2.1. Gravimetric analysis of polyelectrolyte complex

It is known that PEC can be obtained by mixing of interacting components in solution (or by melting) or by matrix poymerization. Figure 5.2 shows the relation between mass of the precipitate formed by mixing the PSP solution with the PABCl solution.

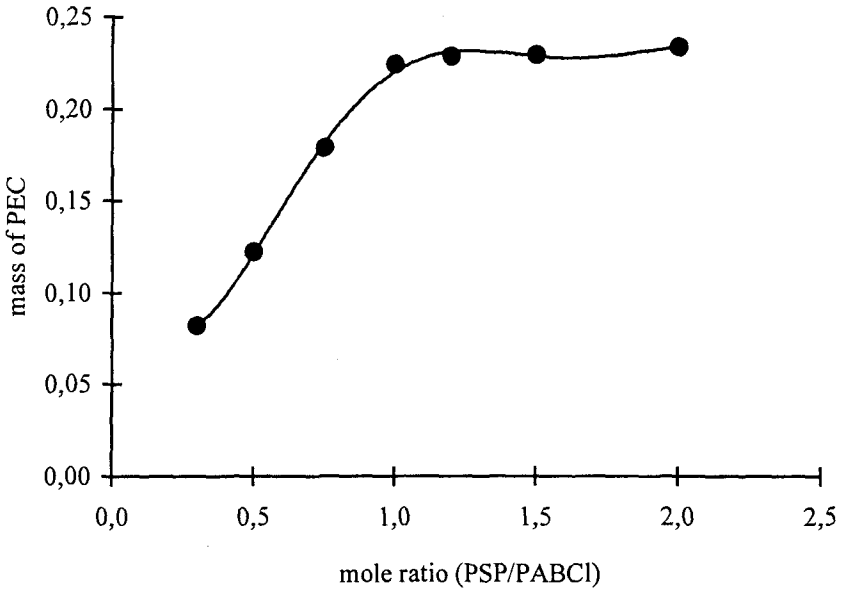


Figure 5.2. Relation between mass of PEC and the mole ratio (PSP/PABCl).

The amount of precipitate is proportional to the amount of PSP added up to a certain PSP/PABCl mol ratio, further it remains constant and the complex keeps its composition, 1:1.2, at any mixing ratio. The excess of PSP does not take part in further formation of the complex. This situation does not depend completely upon the reverse mixing procedure.

5.2.2. Analysis of Supernatant Liquids

The results of UV and volumetric analysis of supernatant liquids of PSP-PABCl complex are shown in Tables 5.6 and 5.7, respectively.

Table 5.6. UV analysis of supernatant liquids.

Mole ratio PSP/PABCl	Concentration of PABCl $x10^5$ ($molL^{-1}$)	Percentage of bounded PABCl (%)
0.8	8.72	82.56
1.0	6.91	86.18
1.2	4.53	90.94
1.5	3.84	92.32
2.0	3.62	92.76

Initial concentration of PABCl is $5x10^{-4}$ $molL^{-1}$

Table 5.7. Volumetric analysis of supernatant liquids for chloride ion.

Mole ratio PSP/PABCl	Moles of Cl^- in supernatant $x10^4$	Moles of PABCl in complex $x10^4$	Mass of PABCl in complex(g)	Percentage of bounded PABCl (%)
0.8	6.048	6.048	0.105	76.1
1.0	6.277	6.277	0.109	79.0
1.2	6.508	6.508	0.113	81.9
1.5	6.738	6.738	0.117	84.8
2.0	6.968	6.968	0.121	87.7

Mass of PABCl in feed is 0.138 g

From the content of unreacted PABCl detected in the supernatant, percentage of PABCl bounded with PSP, and hence the stoichiometry of the complex was determined PSP to PABCl to be 1.2:1.

5.2.2.1. Viscosity Measurements

Table 5.8 compares the measured supernatant liquid and control sample specific viscosities for the PSP-PABCl mixtures.

It shows that for all mixtures, reaction stoichiometry deviates from unity. The departures from stoichiometry are probably due to in the first instance to the existence of unreacted moities in the PEC. If perfect pairing does not occur, those unpaired will be accompanied by their corresponding counterions. The amount of unreacted moities and counterions is relatively small indicating reasonably high interaction.

Table 5.8. Supernatant liquid and control sample specific viscosities for dilute solution PSP-PABCl mixtures

Mixture	Mixture composition mmol/25 ml		Control sample composition mmol/25 ml			η_{sp} of supernatant	η_{sp} of control sample	$\eta_{sp\ supernatant} / \eta_{sp\ control}$
	PABCl	PSP	Ionic excess PABCl	Ionic excess PSP	Maximum supernatant liquid NaCl concentration			
1	0.500	0.500	-	-	0.500	0.52	0.43	1.21
2	0.500	0.250	0.250	-	0.250	1.39	1.43	0.97
3	0.500	0.125	0.375	-	0.125	1.38	1.39	0.99
4	0.125	0.500	-	0.375	0.125	1.66	1.47	1.13
5	0.250	0.500	-	0.250	0.250	1.76	1.43	1.23

5.2.3. Dilute Solution Interactions

The effect of the addition of PSP on the absorbance of PABCl in dilute solution at pH 3 is shown in Figure 5.3 indicating that (a) PABCl and four mixtures (b)-(e).

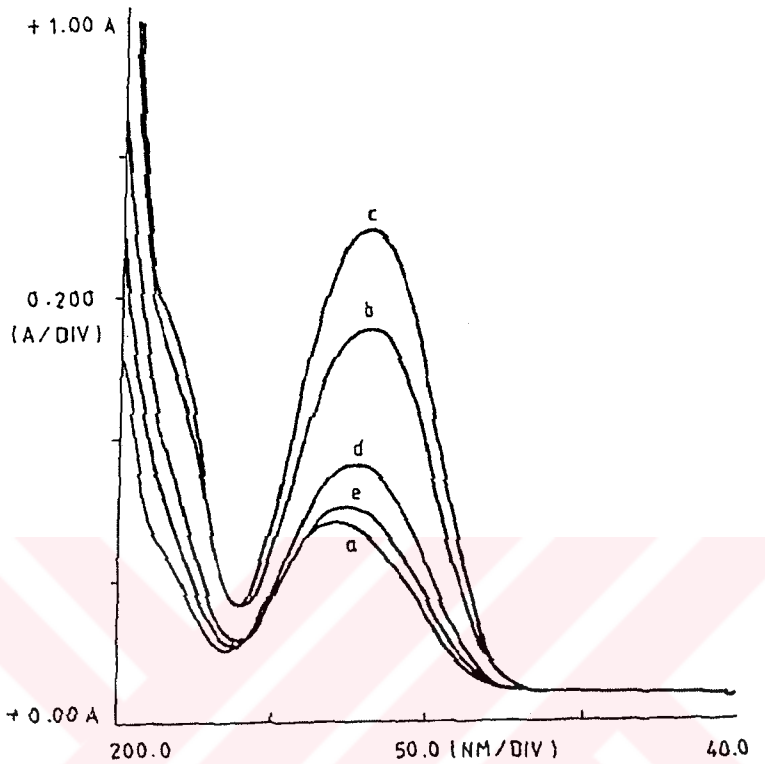


Figure 5.3. Effect of addition of PSP solution on absorbance of PABCl. Mole ratio PSP/ PABCl (b) 1.0:1.0 (c) 1.2:1.0 (d) 0.8:1.0 and (e) 2.0:1.0

The results showed that the PSP component does not have any absorbance peak between 200-1000 nm and the peak at 272 nm in all the curves is due to the interaction of PSP and PABCl.The formation of polyelectrolyte complexes is governed by the characteristics, e.g., position of ionic sites, charge density as well as chemical environments such as concentration, ionic strength, pH etc. In present system, the maximum absorbance has been observed for the mole ratio of 1.2:1 (PSP/PABCl). If the complex formation is completed at a mole ratio of 1.2:1, mixtures (b) and (d) contain excess amount of PABCl. It is known that increasing ionic strength of the solution is unfavorable for PEC formation and PEC composition is not affected significantly by the nature of the salt. In complex mixtures (b) and (d) excess PABCl can behave as salt and affect PEC composition. In complex mixture (e), excess phosphate units are unable to participate in coulombic interaction with

cationic moities of PABCl. PSP is likely to be dissociated to a large extend. Due to mutual repulsion of the charges, PSP will have extended conformation in aqueous medium. In the presence of excess PSP, complex molecules may aggregate and absorbance of the complex mixture decrease.

5.2.3.1. Viscosity Measurements

Figure 5.4 shows the changes of (◊) the specific viscosity (η_{sp}/C_{PSP}) and (●) specific conductance ($\Omega^{-1}cm^{-1}$) of the binary system of PSP and PABCl as a function of the mole ratios of the components PSP/PABCl, in aqueous medium.

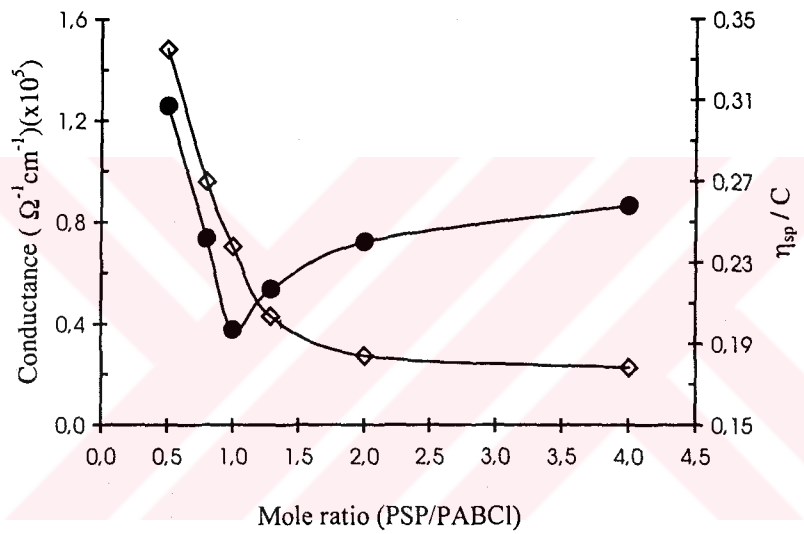


Figure 5.4. Dependence of viscosity (◊) and conductance (●) upon the mole ratio of PSP/PABCl.

It shows that (η_{sp}/C_{PSP}) decreases sharply until the PSP/PABCl mole ratio of 2, and then a slight changes occur with increasing mole. The decrease in the viscosity is caused by complex formation [16,58,64,133]. Dependence of the viscosity upon temperature was also investigated. Results are shown in Figure 5.5. Temperature dependence of the viscosity also confirms the interaction between PSP and PABCl.

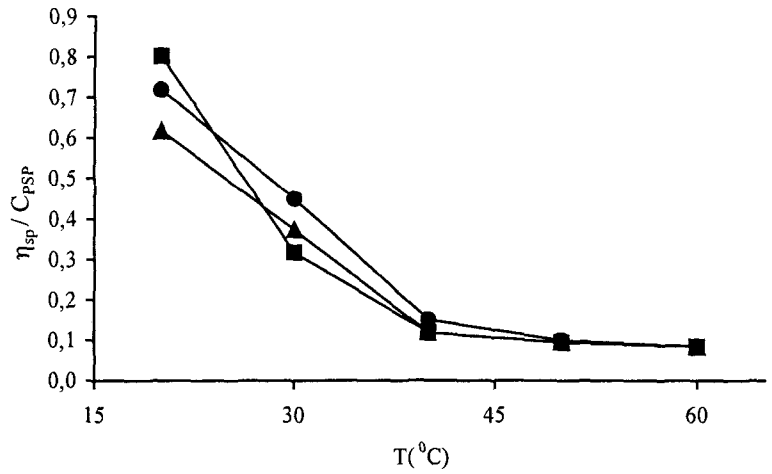


Figure 5.5. Dependence of viscosity of PSP (■) and PABCl (●) and PEC (▼) upon temperature.

5.2.3.2. Conductometric Titrations

The use of conductance measurements to examine the interaction between oppositely charged polyions depends on the change of equivalent conductance versus the concentration of species in the solution [134]. Conductometric titration techniques have been used by other workers to investigate the stoichiometry of PEC formation [1,13,134]. Regarding the present work Figure 5.6 shows the results of conductometric titration for the addition of PSP to PABCl.

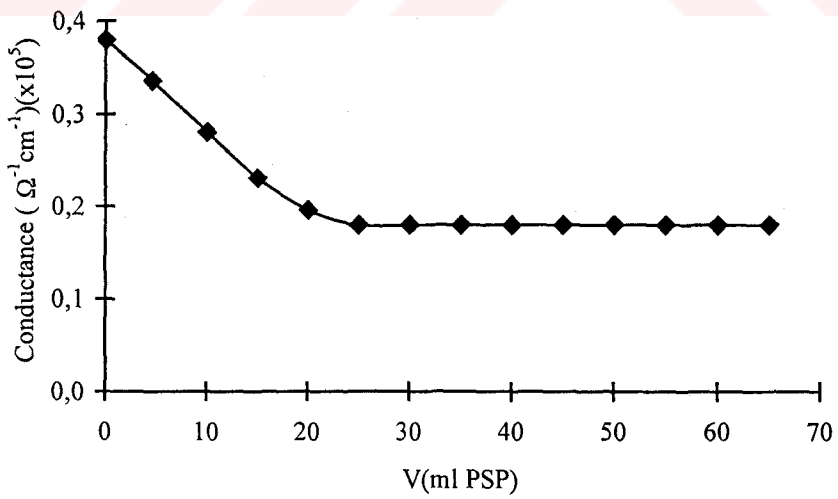


Figure 5.6. Conductometric titration of 30 ml 1x10^{-3} molL^{-1} PABCl with 1x10^{-3} mol L^{-1} PSP.

Conductance falls during the titration until the end point. After the end point, the conductance remains constant. The decreased part of the figure shows the binding of PSP to PABCl with the release of counter ions, then due to the increase in the effective charge density at the domain of components, the reaction between PSP and PABCl slows down, and the coiling of polyion takes place to bring the active functions to mutual position and the arrangement of polyions occurs with the coiling of the polyion chain and the stoichiometry deviates from the unity [135,136]. Figure 5.7 shows the added salt effect on the reaction.

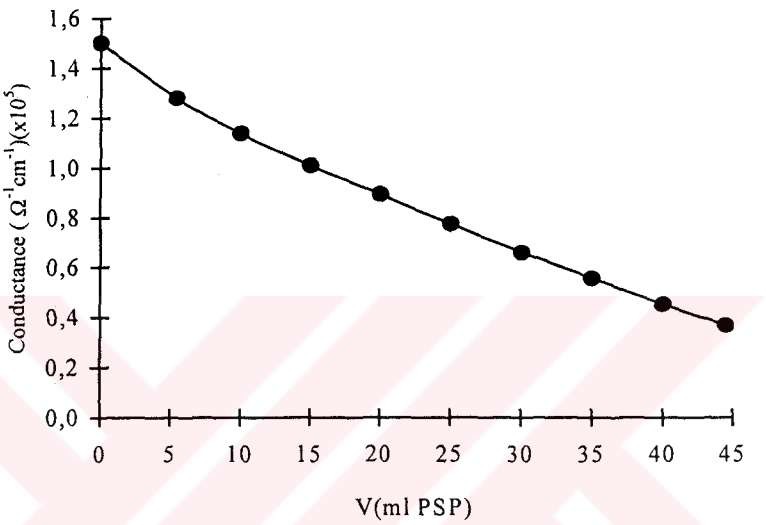


Figure 5.7. Conductometric titration of 30 ml $1x10^{-3}$ $molL^{-1}$ PABCl with $1x10^{-3}$ mol L^{-1} PSP in $1x10^{-2}$ $molL^{-1}$ NaCl.

5.2.4. Breakdown of Polyelectrolyte Complex

Breakdown of PEC (PSP-PABCl) often requires a more complex (often ternary) solvent. Table 5.9 shows the solvents to dissolve the present system.

Table 5.9. Solvents to dissolve PEC.

	Solvents			
Solubility	DMF	DMSO	Ethanol	Water
PEC	+	+	-	-
PSP	-	-	-	+
PABCl	+	+	+	+

(+) soluble (-) insoluble

With regard to suppression of PEC formation, the solutions each comprised 5 ml of 0.1 $molL^{-1}$ aq.components. Complete clarity was obtained for [NaCl] $\geq$ 2 $molL^{-1}$, complex formation between PSP and PABCl does not occur. The added NaCl in the lower concentration than 2 $molL^{-1}$ suppressed the complex formation due to the common ion effect.

We have checked the ionic strength on the critical pH value for the system which contains 5 ml, 0.1 $molL^{-1}$ PABCl and 5 ml, 0.1 $molL^{-1}$ PSP. In the absence of NaCl, the turbidity of the system decreases with increasing pH beginning from 2.65. Complete dissolution of the complex is observed at pH 4.59 visually, whereas in the presence of 0.1 $molL^{-1}$ NaCl, dissolution is observed at pH 3.14.

5.2.5. Potentiometric Titration of Polyelectrolyte Complexes in Nonaqueous Medium

0.1893 g PABCl and 0.2334 g PSP-PABCl complex dissolved in 25 ml of DMSO separately and titrated with 0.1 $molL^{-1}$ TBuAH. Results are shown in Figure 5.8.

As shown in Curve a, the pH of the solution changes quite slowly until just before the equivalence point is reached. At around the equivalence point the pH rises sharply. Beyond the equivalence point, the pH again changes quite slowly as excess TBuAH is added. pK_a values of PABA are 2.42 and 4.87 for [COOH] and [NH_3^+], respectively. Using pK_a values, the calculated H^+ concentration at equivalence point is 0.039 $molL^{-1}$ in DMSO for PABCl. 4 ml of TBuAH solution is used at the end point, so concentration of H^+ is equal to 0.032 $molL^{-1}$ which is lower than the calculated value. It is difficult to conclude that this difference can be assumed a reaction between PABCl and DMSO.

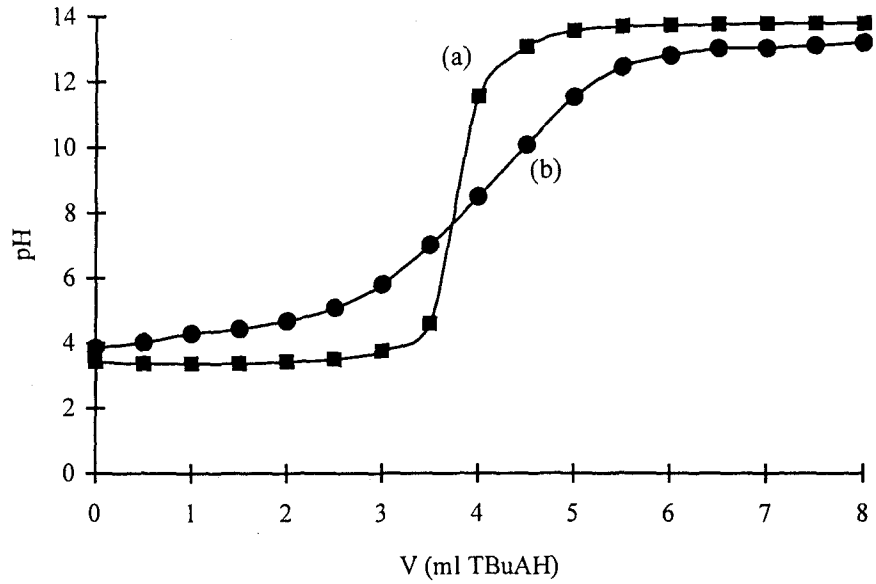


Figure 5.8. Potentiometric titration of PABCl (a) and PEC (b) with 0.1 $molL^{-1}$ TBuAH.

As shown in curve (b), in the PEC solution, the theoretical H^+ concentration is 0.012 $molL^{-1}$ at the equivalence point and 0.015 $molL^{-1}$ at the end point. This difference also is not meaningful whereas the slopes of two curves (a, b) at around equivalence and end point are rather different.This result suggest that an interaction between PSP-PABCl complex and DMSO solvent might occur via hydrogen bonding. Tsuchida and coworkers [137] investigated the complex formation between poly(methacrylic acid) (PMAA) and poly(vinylpyrolidone) (PVP) in water and DMSO and they showed that PMAA-PVP complex occurs in DMSO by strong hydrogen bond formation between the PMAA and DMSO.

5.2.6. Polyelectrolyte Complexes-Metal Interaction

Figure 5.9 shows the potentiometric titration of PEC (PSP-PABCl) considering ionic strength (0.01 $molL^{-1}$ $NaClO_4$) in the absence and the presence of Cu (II). The decrease in the initial pH and the difference between the end points of titration curves indicated that, an interaction can be assumed between PEC and Cu (II).

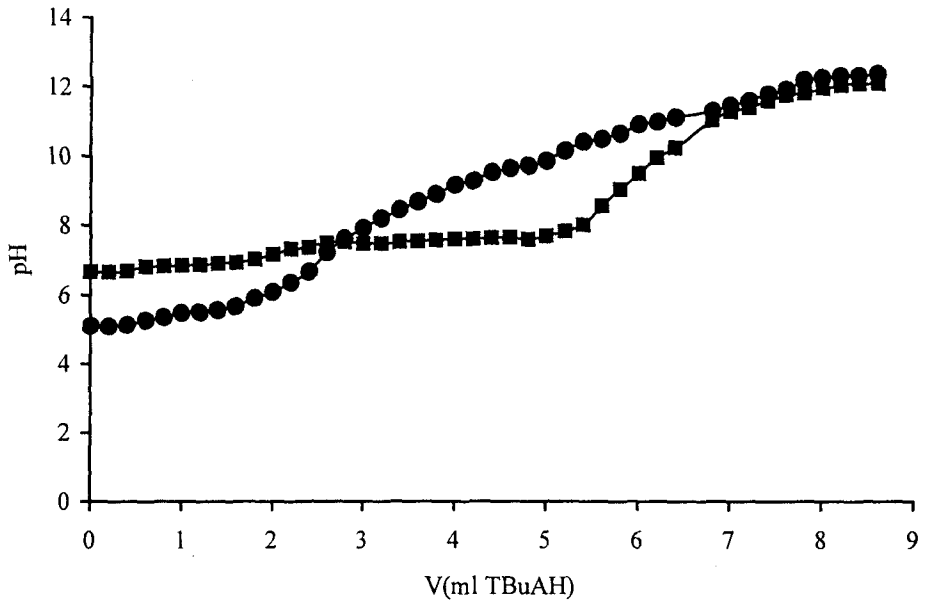


Figure 5.9. Potentiometric titration of PEC with ionic strength of 0.01molL^{-1} $NaClO_4$, in the absence (•) and the presence (■) of 0.04 molL^{-1} Cu (II) with 0.1 molL^{-1} TBuAH.

5.3. Interaction Between Poly(4-vinyl pyridine) and 4-amino benzoic acid

The nature of interaction between P4VP and 4-amino benzoic acid was established by IR spectroscopy. Figure 5.10 shows the IR spectrum of P4VP. P4VP has several absorption bands due to the ring distortion vibrations, which are similar to benzene [77]. P4VP exhibits a pyridine ring-stretching band at 1597 cm^{-1}. The pyridine ring mode is different from the pyridinium ring mode. The most remarkable bands are the characteristic modes of the pyridine ring at 1597, 1493 and 993 cm^{-1} for P4VP. The band at 1597 cm^{-1} can shift towards higher wavenumbers due to the formation of effective crosslinking and complete pyridine protonation.

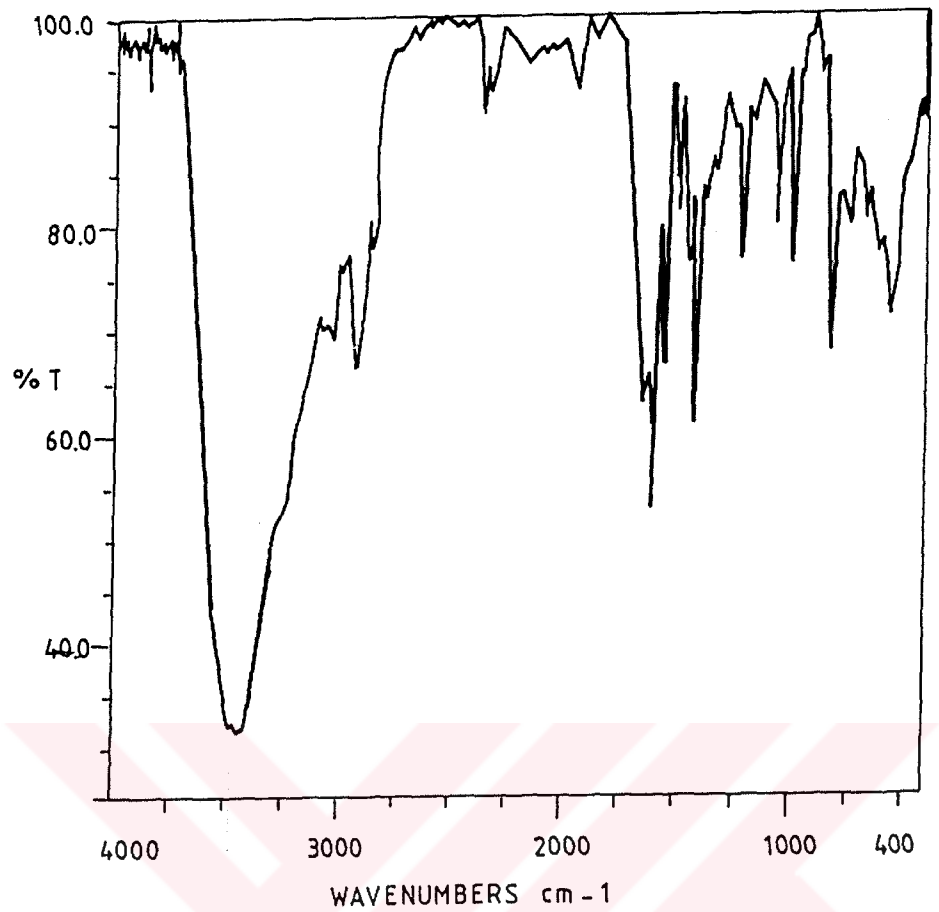


Figure 5.10. IR spectrum of P4VP.

Figure 5.11 shows the IR spectrum of pure 4-amino benzoic acid.The absorption bands around 3000 cm^{-1} and the absorption at 1702 cm^{-1} indicate that the carboxyl group in pure 4-amino benzoic acid is not in free but in associated state. Bands in the 1200-1750 cm^{-1} region characteristics of RCO_2H or RCO_2^- are importance in establishing the state of ionization of the RCO_2H.

Figure 5.12 shows the IR spectrum of PEC.

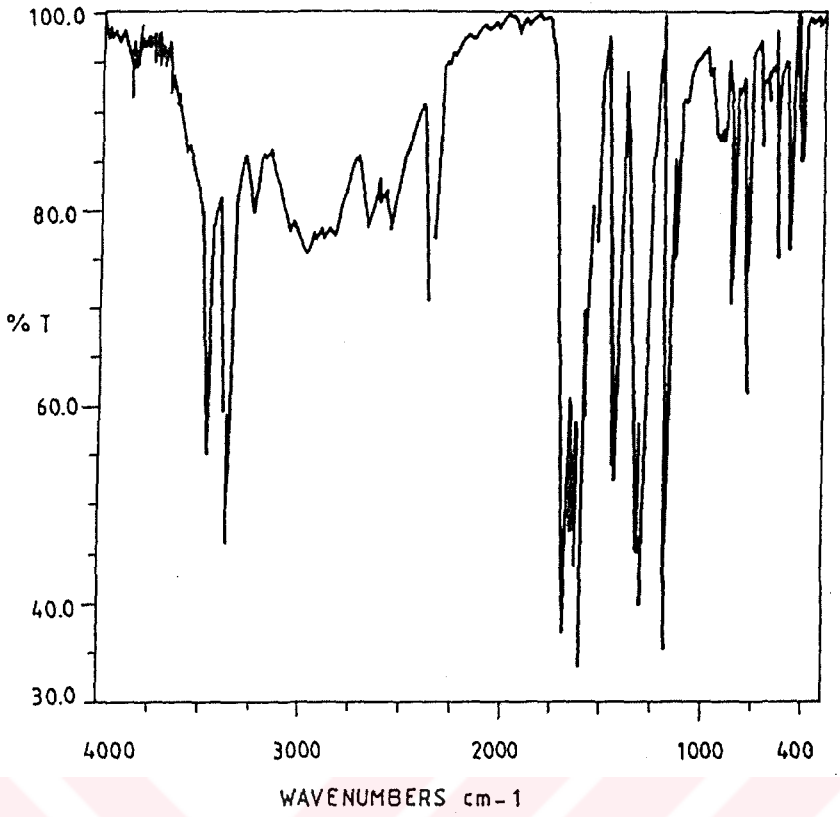


Figure 5.11. IR spectrum of 4-amino benzoic acid.

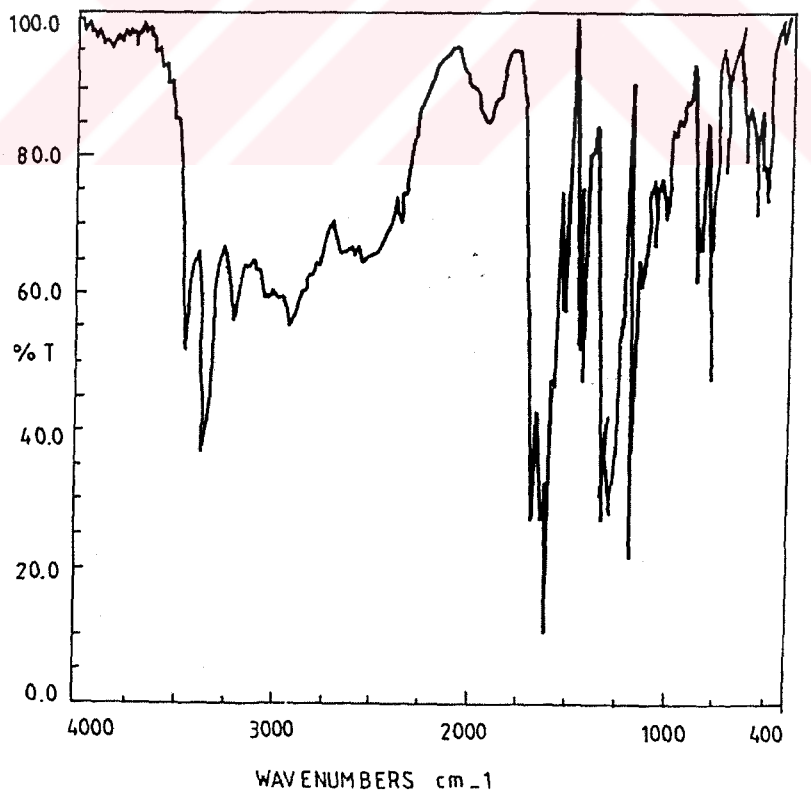


Figure 5.12. IR spectrum of PEC (P4VP-PABA).

The C= O stretching vibration appeared at 1702 cm^{-1} indicates that carbonyl group is in associated state. A carbonyl band near 1700 cm^{-1} is characteristic of a unionised carbonyl group whereas a band near 1600 cm^{-1} is characteristic of COO^- group [138]. The O-H stretching vibration appeared at 2570 and 1931 cm^{-1}, which shows that hydroxyl group, forms stronger hydrogen bond than in pure 4-amino benzoic acid. Furthermore, there is almost no change of positions of the absorption peaks from 1650 cm^{-1} to 1300 cm^{-1} in Figure 5.13 in comparison with the others, which implies that the carbonyl group of 4-amino benzoic acid in the PEC is not ionised, as well as the pyridine group of P4VP. These results support the concept that the PEC is not formed via electrostatic attraction but hydrogen bonding. In the following scheme;

$$\underset{(a)}{A\text{-}H + B} \Leftrightarrow \underset{(b)}{A\text{-}H.....B} \Leftrightarrow \underset{(c)}{(A....H....B)} \Leftrightarrow \underset{(d)}{A...H\text{-}B} \Leftrightarrow \underset{(e)}{A^- + H^+ B} \qquad (5.3)$$

The process starts with free base (B) and a free acid (AH) (depicted as (a) above). For weak and moderately strong hydrogen bonds, the hydrogen atom is located closer to one atom or the other (depicted as (b) and (d) above). As the strength of the hydrogen bond increases and the A....B length decreases, the hydrogen atom is not so clearly identified as more strongly associated with one atom or the other (depicted as (c) above). Benzoic acids (pK_a ~ 4) form bonds with pyridine [138-140]. For a complex of phenol (pK_a =10) and pyridine, the O-H stretching band appears at 3010 cm^{-1}, which indicates weak hydrogen bonds [139]. pK_a value of 4-amino benzoic acid is 2.42, it is much stronger than benzoic acid so we can say that it can form strong hydrogen bond with P4VP. Figure 5.13 shows the ^{13}C NMR spectrum of PEC. As can be seen from the spectrum, the peak at 171 ppm indicates the participation of the carbonyl group of 4- amino benzoic acid in the formation of the complex.

The result of T_g studies on P4VP and PEC are given in Figure 5.14. As shown in Figure 5.14 P4VP and PEC exhibit well-defined glass transitions (379 K and 337 K, respectively).

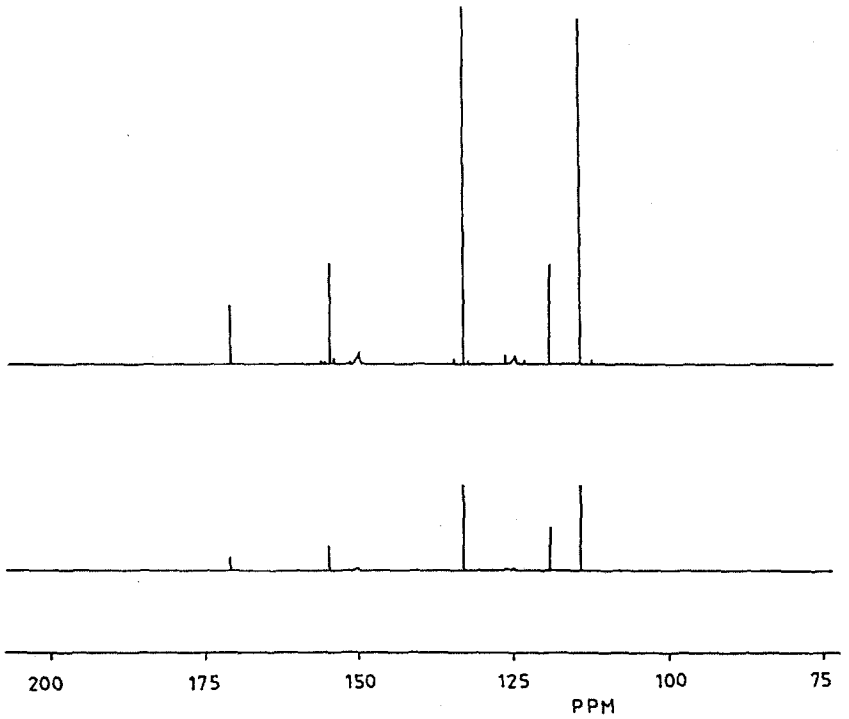


Figure 5.13. ^{13}C NMR spectrum of PEC (P4VP+PABA).

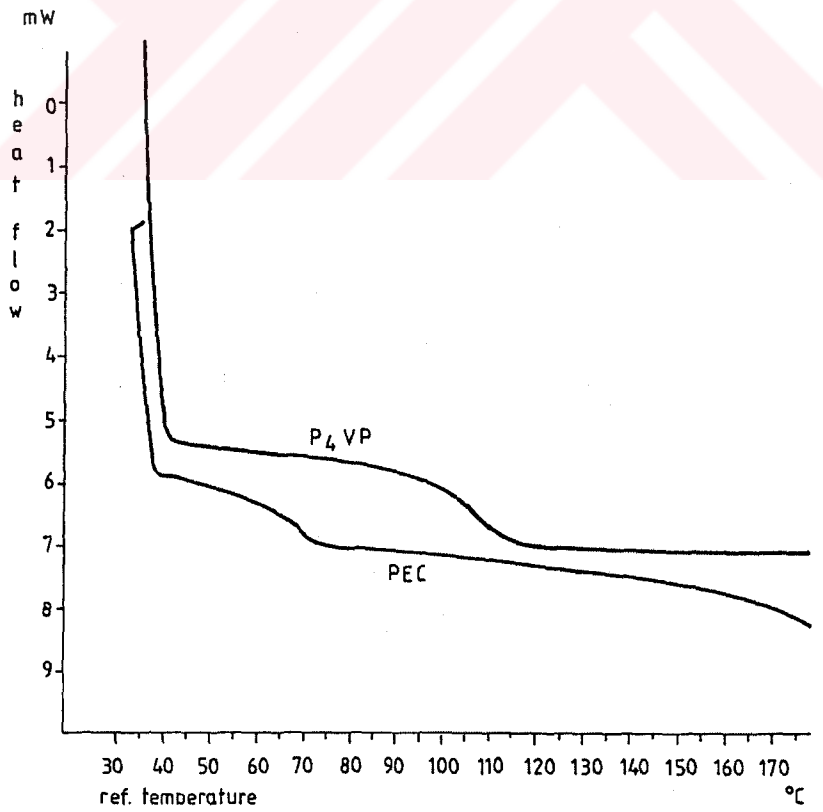


Figure 5.14. DSC curves for P4VP and PEC (P4VP+PABA).

The T_g value of amorphous component (P4VP) decreases with addition of crystalline component (PABA). Due to addition of crystalline component, structure of P4VP can be changed and PABA is probable to reveal plasticizing effect on the P4VP so that T_g value of PEC decreases due to this effect.

Protonation constants of PEC (P4VP-PABA) and the stability constants of PEC-Cu^{2+} have been determined by potentiometric method at 293 K. The protonation constants of PEC were determined by the Irving-Rossotti pH titration technique in ethanol+water solution [141]. Typical titration curves obtained as shown in Figure 5.15.

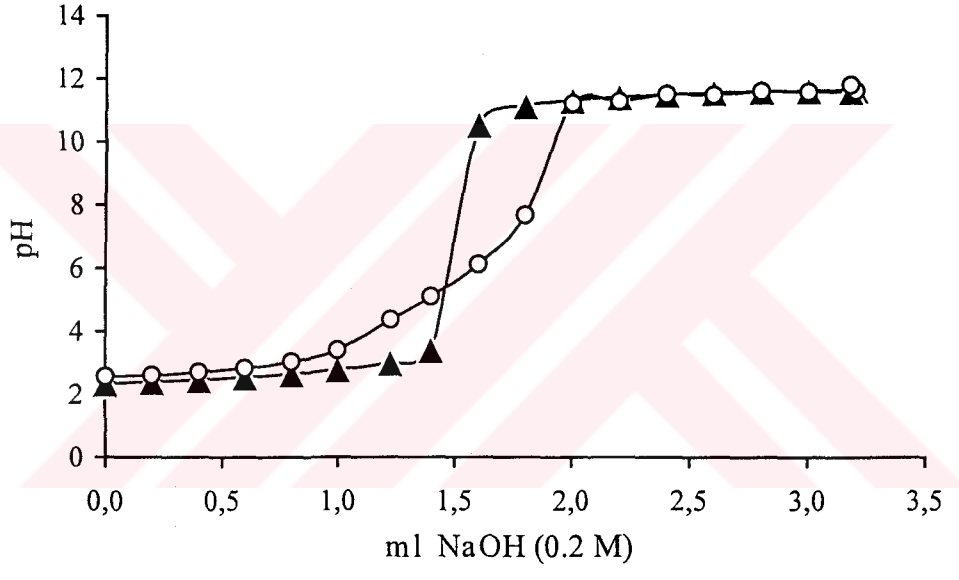


Figure 5.15. Potentiometric titration of 25 ml solution, (a) which contains 3 ml of 0.1 $molL^{-1}$ $HClO_4$ + 2.5 ml of 1 $molL^{-1}$ $NaClO_4$ + 12.5 ml of ethanol and 7 ml of water (▲) (b) same solution composition, in the presence of 0.0217 g PEC, with 0.2 $molL^{-1}$ NaOH (o).

Degree of formation of proton-ligand complexes (n_A) was calculated using Equation 5.4.

$$n_A = \left\{ yT_L^0 + \frac{(v_1 - v_2)(N + E^0)}{V_0 + v_1} \right\} \Big/ T_L^0 \qquad (5.4)$$

Where V_0 is the initial volume, E^0 represents the mineral acid concentration, T^0 is the total ligand concentration, v_1 and v_2 are the volumes, N is the concentration of the standard base, consumed to reach certain pH values in the presence and absence of ligand, respectively [141]. Figure 5.16 shows the graphical determination of protonation constants by Irving –Rossotti method. From the n value corresponding to the half value points of the curve, logarithm of protonation constants were calculated to be Log K_1 = 6.45, Log K_2 = 4.30, Log K_3 = 2.58 .

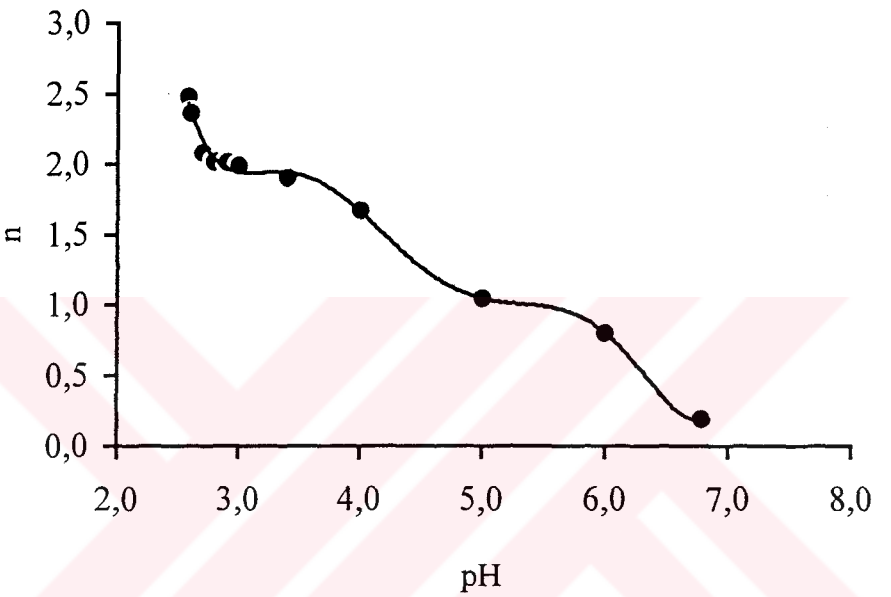


Figure 5.16. Graphical determination of protonation constants of PEC from the half value points.

From the titration curve of 5.17, the formation constants of PEC- Cu^{2+} complexes were calculated using Calvin and Melchior's simple method [142].

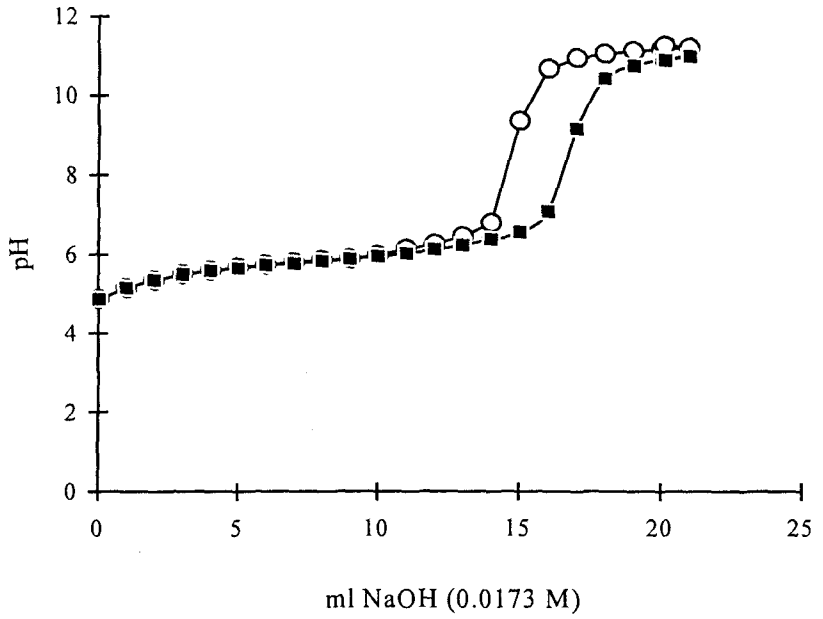


Figure 5.17. Potentiometric titration of (a) 25 ml solution which is prepared as dissolution of 0.065 g PEC (P4VP+PABA) in 12.5 ml of ethanol + 2.5 ml of 1 $molL^{-1}$ $NaClO_4$ and 10 ml of water (o) (b) the same solution composition, in the presence of 0.01 $molL^{-1}$ $CuSO_4$, with 0.0173 $molL^{-1}$ NaOH (■).

The horizontal distances between two titration curves give the amounts of standard solution equivalent to the hydrogen ions liberated during the formation of the complex PEC-Cu^{2+} according to Equation 5.5 where

$$\bar{n} = \frac{[L_{bound}]}{C_M} = \frac{(a - a_0)C_{HL}}{C_M} \qquad (5.5)$$

L_{bound} : Concentration of bound ligand.

a_0: Degree of neutralization of an acid at a given pH.

a: Degree of neutralization of an acid at a given pH in the presence of metal ion.

C_{HL}: Concentration of an acid in titration solution.

C_M: Concentration of metal ion in titration solution.

The free ligand concentration can be calculated as follows;

$$[L] = \frac{C_{HL} - (a - a_0)C_{HL}}{\alpha_{L(H)}} \qquad (5.6)$$

where $\alpha_{L(H)}$ represents the degree of dissociation and it can be calculated as follows;

$$\alpha_{L(H)} = 1 + [H^+]K_1 + [H^+]^2 K_1K_2 + [H^+]^3 K_1K_2K_3 \qquad (5.7)$$

The pH difference in standard solution consumption read directly from the curve and the calculated bound ligand (PEC) concentration [L_{bound}], the average ligand number (n) and the free ligand concentration [L] are summarised in Table 5.10. The $Log\alpha_{PEC(H)}$ values belonging to various pH values are calculated from the titration data.

The formation curve constructed from the (n) and the pL ($-Log_{[L]}$) values calculated, is shown in Figure 5.18. The approximate stability constant is calculated using n value from the curve according the 'half-value point' is 1.59×10^3.

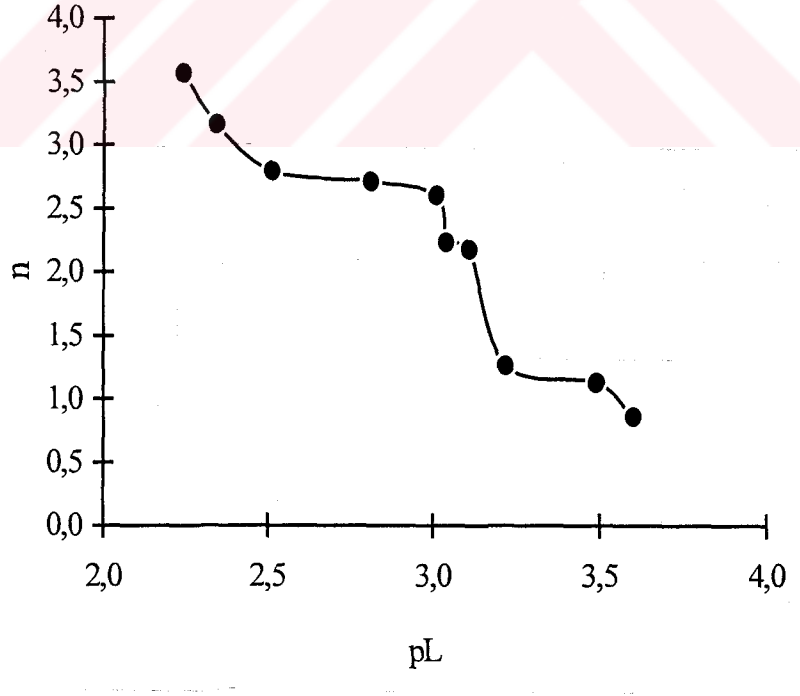


Figure 5.18. Determination of stability constants of PEC- Cu (II) complex by half value points.

Table 5.10. Calculation of the points of the formation curve for PEC-Cu(II) complexes, from the data of titration curves in Figure 5.17.

pH	0.01730 M NaOH (ml)	$(a - a_0)C_{PEC} = [L_{bound}]$ x10^{-4}	$n = [L_{bound}] / C_{Cu^{2+}}$	$Log(C_{PEC} - [L_{bound}]) - log\ \alpha_{(PEC(H))} = Log_{(L)}$
5.12	0.50	2.12	0.86	-3.60
5.23	0.65	2.78	1.13	-3.49
5.50	0.73	3.11	1.26	-3.22
5.64	1.25	5.36	2.17	-3.11
5.71	1.28	5.50	2.23	-3.04
5.76	1.50	6.42	2.60	-3.01
6.00	1.57	6.69	2.71	-2.81
6.50	1.61	6.88	2.79	-2.51
7.00	1.82	7.81	3.16	-2.34
9.00	2.06	8.81	3.57	-2.24

$C_{Cu^{2+}} = 2.47 \times 10^{-4}$ molL^{-1} $C_{PEC} = 6.62 \times 10^{-3}$ molL^{-1}

The concentrations of PEC and Cu are calculated by taking the solution volume 40.5 ml, corresponding to consumption of 15.5 ml of titrant.

5.4. Irradiation Effects on Poly(4-vinylpyridine)

Poly(4-vinylpyridine) was irradiated to obtain advanced cross-linked structure. Highly cross-linked polyelectrolytes gives well-established polymer gel and of which forms interpolymer complexes with linear–chained macromolecules. The formation of intermolecular complexes between the linear polymers P4VP and PSP was throughly investigated [136]. The complexation phenomena in the swollen P4VP in the aqueous solution of the oppositely charged linear PSP was tried to examine.

5.4.1 Gel Determination

The formation of intermolecular crosslinks is one of the most important changes brought about radiation, since crosslinking of polymers leads to beneficial changes in some of their properties, such as heat resistance, the degree of crosslinking etc. Therefore, the gelled part, ie. the insoluble part of P4VP films having different

degrees of crosslinking was determined. Results are given in Figure 5.19 that shows the relation between the gel percent and irradiation dose for P4VP films.

Initially the gel percent increase with increasing irradiation dose up to 0.61 MGy, at higher doses increase in gel percent is small. The P4VP film, which was subjected irradiation with a dose rate of 1.84 MGy, was broken during irradiation process. The irradiation environment, in the presence of oxygen during radiation markedly affected radiation resistance. When irradiation is carried out in the presence of oxygen, additional chemical reactions can occur. Thus, the gel percent of P4VP film subjected irradiation at a dose of 1.84 MGy was bigger than the film which was subjected irradiation with a dose rate of 2.19 MGy.

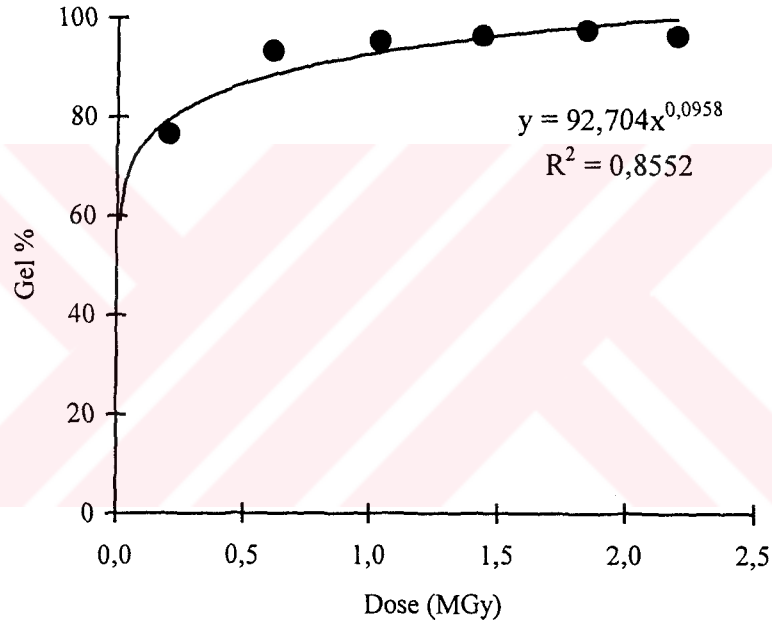


Figure 5.19. Gel percent of P4VP with irradiation dose (The solid curve is the best fitting curve to the experimental data).

Generally, the chemical change occuring in the polymeric substance is directly proportional to the active sites formed. The efficiency of such sites to initiate crosslinking process is higher in the amorphous region than in the crystalline region because of the active sites higher mobility in former case. Therefore, the number of radicals formed by irradiation at first increases as the dose increases. At higher doses, no more active sites are formed and the constant concentration of radicals gives also a curvature relationship for degree of crosslinking with dose [143,144].

Much effort is expended on measuring the relationship between radiation dose and gel fraction, since this determines the efficiency of crosslinking, the G value of crosslinking, $G_{(x)}$ and the G value of scission, $G_{(s)}$. In many instances, radiation induces simultaneous crosslinking and scission reactions. In these cases, the yields for each reaction can be determined by Charlesby-Pinner relationship [145].

$$s + s^{1/2} = \frac{50N}{M_n} G_x \frac{1}{D} + \frac{G_S}{G_x} \tag{5.8}$$

Where s =sol fraction of the irradiated polymer, M_n = number average molecular weight of polymer prior to irradiation, D = absorbed dose, G_s = scission yield and G_x= crosslinking yield. To permit the calculation of crosslink yields, a determination of scission concurrent with crosslinking is necessary. Results are shown in Figure 5.20 and Table 5.11 for P4VP films. In Figure 5.21, $s+s^{1/2}$ is plotted against 1/dose for irradiated P4VP films.

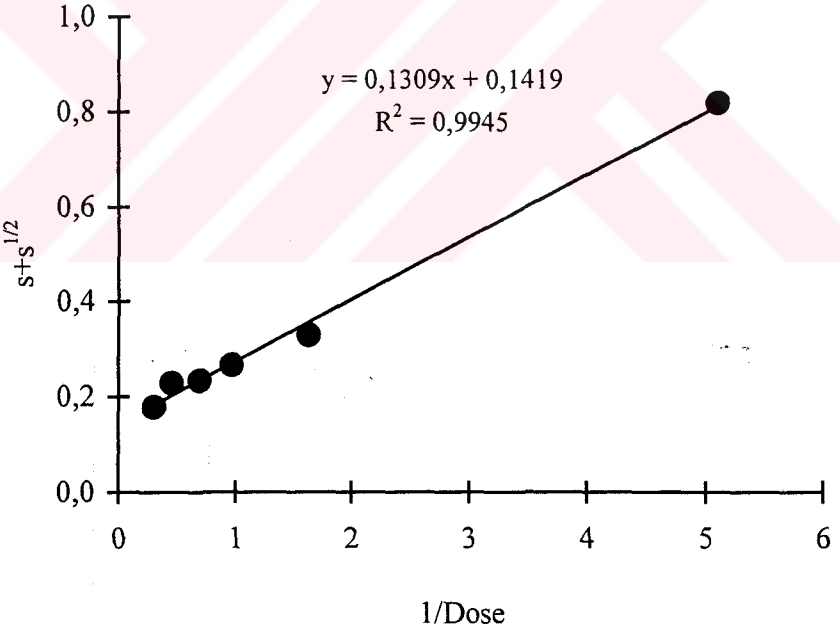


Figure 5.20. Solubility of irradiated P4VP films in ethanol as a function of the reciprocal of dose.

Table 5.11. Determination of sol-gel fractions of irradiated P4VP films by UV spectroscopy.

Sample No	Dose (MGy)	1/Dose	w_{sol} (g)	w_{gel} (g)	$(w_{sol}+w_{gel})^a$ (g)	$s_{sol\ fraction}$	$s^{1/2}$	$s+s^{1/2}$	$g_{gel\ fraction}$
1	0,196	5,102	0,285	0,932	1,217	0,284	0,533	0,817	0,766
2	0,614	1,629	0,078	1,076	1,154	0,068	0,260	0,328	0,932
3	1,027	0,973	0,045	0,904	0,950	0,048	0,218	0,266	0,952
4	1,432	0,698	0,026	0,661	0,687	0,038	0,195	0,233	0,962
5	1,841	0,543	0,020	0,798	0,818	0,024	0,155	0,179	0,976
6	2,188	0,457	0,035	0,900	0,935	0,037	0,192	0,229	0,963

[a] = initial weight of sample

Extrapolation to 1/dose = 0 gives value for G_s / G_x , the scission to crosslinking ratio, of 0.142 for irradiated P4VP films.

Extrapolation to complete solubility ($s+s^{1/2} = 2$) permits an estimate of the gel points. For a calculation of both crosslinking and scission yields, the gel point dose, r_g, and the scission to crosslinking ratios may be substituted in Equation 5.9 [146].

$$\frac{w}{M_w} = r_g\left(G_x - \frac{G_s}{2}\right) \qquad (5.9)$$

in which w= molecular weight of repeating unit, M_w= molecular weight of polymer prior to radiation, $r_g = 7.06\times10^{-4}$ MGy. For P4VP, $M_w = 14.9 \times 10^4$, substituting $G_s / G_x = 0.142$ gives; $\frac{w}{M_w} = r_g(0.929G_x)$ and G_x is found 0.011. The scission yield is $G_s = 0.142\ (0.011) = 1.56\times10^{-3}$. In literature polystyrene (PS) was chosen for the study because it was easy to prepare and characterize as a linear polymer and it crosslinked by radiation with few side reactions. On the basis of some literature values for G_x and G_s, namely, approximately 0.043 and 0, respectively, for irradiation in vacou. G_x decreased from 0.043 in vacuo to 0.022 in air, there being a concominant increase in

G_s from 0 to 0.022 [105]. In the γ radiation induced crosslinking of PS in vacuo Shimizu and coworkers [147] investigated that the gel fraction increased with increasing irradiation time by the irradiation beyond the critical time for incipient gel formation and the rate of gel formation decreased with time. They found that at 30 ^{0}C G_x=0.035 and G_x =0.01 when temperature was increased to 70 ^{0}C, G_x and G_s values were 0.042 and 0.051, respectively. Parkinson et al. [109] described measurements of crosslinking in PS with γ- radiation and with the mixed γ- neutron field of a reactor. G_x value for PS is smaller than the values for P4VP.

The vinylpyridine monomers are somewhat more reactive than styrene; this observation is consistent with the methyl affinities of the respective monomers. Methyl affinity (relative reactivity of monomer towards methyl radical) of styrene and 4-vinylpyridine is 792 and 1360 respectively.

5.4.2 Swelling Measurements

Figure 5.21 represents the ethanol uptake of P4VP as a function of dose. It can be seen that the ethanol uptake decreases with increasing dose in accordance with the increasing degree of crosslinking, which normally results in lower degree of swelling [108,148].

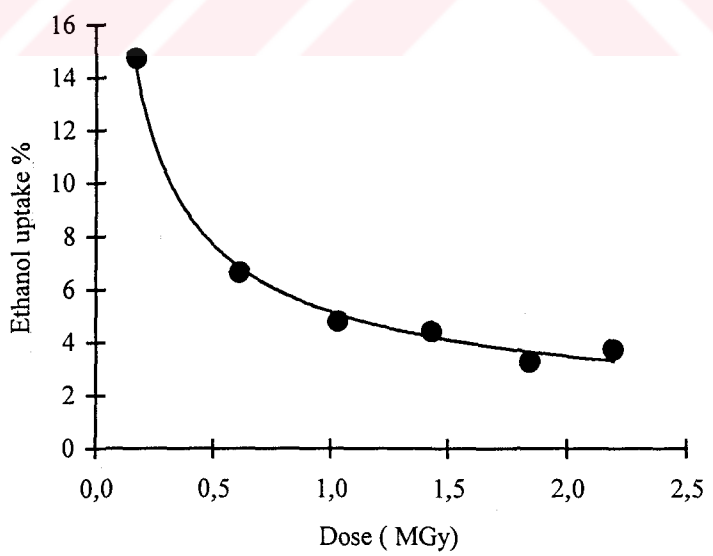


Figure 5.21. Ethanol uptake of P4VP gels as a function of irradiation dose.

5.4.3. Determination of M_c Values of Gels

The gels thus prepared were characterized with respect to their swelling properties and network structures. One of the basic parameters that describes the structure of a gel network is the molecular weight between crosslinks, M_c, for swollen networks. This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical crosslinks, physical entaglements, crystalline regions or even polymer complexes [148-151]. Several theories have been proposed to calculate the molecular weight between crosslinks in a gel. Probably the most widely used of these theories is that of Flory and Rehner [152,153]. This theory describes the equilibrium swelling characteristics of a crosslinked polymer system where the polymer chains have reacted in a solid state. The theory deals with neutral polymer chains within the polymer gel. From the swelling expression (4.5) the average molecular weight between consecutive crosslinks, M_c can be expressed by Equation 5.10. This equation has been widely used to characterize a variety of networks. It was used when the network was prepared from polymer, not from monomer or monomer mixtures.

$$\frac{1}{M_c} = \frac{2}{M_n} - \bar{v}/V_1 \frac{\left[\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2\right]}{\left[V_{2m}^{1/3} - V_{2m}/2\right]} \qquad (5.11)$$

Here M_c is the number average molecular weight of starting polymer, $\bar{v}$ is the specific volume of polymer, V_1 is the molar volume of the swelling agent, V_{2m} is the polymer volume fraction in the equilibrium-swollen system and χ is the Flory polymer-solvent interaction parameter. χ is 0.49 for P4VP-ethanol system [122], V is 58.3 gml^{-1} for ethanol. The M_c values thus determined from Equation 5.10 are given in Table 5.12. The results obtained show that the average molecular weight between crosslinks decreases by increasing dose.

Table 5.12. Values of M_c for P4VP gel systems.

Dose (MGy)	M_c (g mol^{-1})	q_v
0.20	107269	19.7
0.61	49965	7.0
1.03	38441	5.8
1.43	34859	5.3
1.84	20127	3.9
2.19	26470	4.5

When a non-ionic polymeric network is placed in a swelling agent, there are two contributions to the free energy of the system, mixing and elastic-retractive free energies as expressed as ΔG_{mix} and ΔG_{el}, respectively [154]. It is assumed that the change in total free energy is the sum of ΔG_{mix} and ΔG_{el}, thus

$$\Delta G = \Delta G_{mix} + \Delta G_{el} \tag{5.11}$$

The state of equilibrium is obtained when the two changes balance each other. Mathematically this state is expressed as;

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{T,P} = \left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{T,P} + \left(\frac{\partial \Delta G_{el}}{\partial n_1}\right)_{T,P} = 0 \tag{5.12}$$

Where n_1 is the number of molecules of swelling agent, subscripts T, P indicate that the differentiantions made at constant temperature and pressure.

Performing the differentiations indicated in Equation 5.12;

$$\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2 + \frac{V_1 \rho}{M_c}\left(V_{2m}^{1/3} - V_{2m}/2\right) = 0 \tag{5.13}$$

or, adopting the terminology

$$\frac{V_1\rho}{M_c} = N^{-1} \tag{5.14}$$

Where N is the number of segments in a network chain, ρ is the density of polymer network.

$$\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2 = -N^{-1}\left(V_{2m}^{1/3} - V_{2m}/2\right) \tag{5.15}$$

The left hand member in this equation represents the lowering of the chemical potential owing to mixing of polymer and swelling agent; that on the right gives the increase from the elastic region of the network. As expressed before (Eq. 4.10), at swelling equilibrium, $1/V_{2m}$ may be replaced by q_v. At large M values of 10000 or more, q_v in a good solvent will exceed 10. Then $V_{2m}/2$ is considerably smaller than $V_{2m}^{1/3}$ and can be neglected. Also higher terms in the series of expansion of the first term member of Equation 5.13 may be neglected. The swelling equilibrium equation may then be solved for $V_{2m} = 1/q_v$. The Flory- Rehner equation relating volume swelling ratio to density of crosslinks has been simplified by Charlesby [155] to the form ;

$$q_v^{5/3} = N^{-1}(1/2 - \chi) \text{ or } q_v = \left(\frac{0.5 - \chi}{N}\right)^{3/5} \tag{5.17}$$

Since M_c is proportional to the reciprocal of dose, a log- log plot of q_v vs 1/dose should have a slope of 0,6. The data are presented in this manner in Figure 5.23 with the line constrained to slope of 0,64 for P4VP samples.

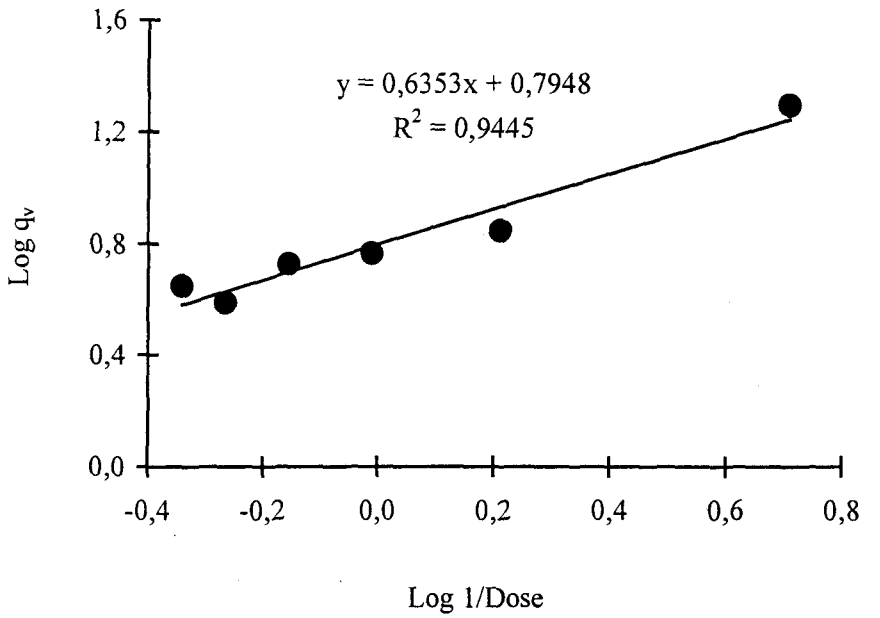


Figure 5.22. The log- log plot of the equilibrium volume swelling ratio q_v of the P4VP gels versus reciprocal of dose.

5.4.4. Quaternization of P4VP Film

Quaternization percent was calculated as 109 % using expression (4.11). Deviation from theoretical value in HCl percent may be partially due to some occluded unwashable HCl in the film.

5.4.5. Interaction of PSP with P4VHCl Gel

The quaternized samples were immersed in water during 24 h in order to achieve equilibrium state. The K_s values of P4VPHCl gel was 130 and a sharp contraction in the gel volume was easily detected by naked eye. Bekturov et al. [155] was observed the same phenomena in the interaction of the oppositely charged polymer hydrogel with linear polymer. Figure 5.24 shows the dependence of K_s for P4VPHCl gel on the concentration of PSP.

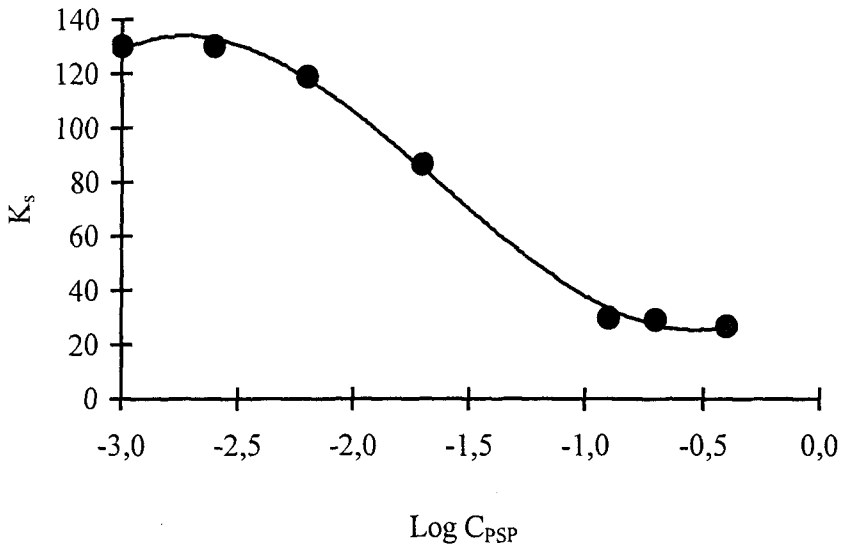


Figure 5.23. Depence of Ks of P4VPHCl gel on concentration of PSP solution.

The result shows that concentration changes of PSP within the certain interval induces a sharp decrease in the K_s value. For the contractration of the gel two possible reason may be suggested;

1) The osmotic deswelling of the gel in the polymer solution (no complex formation)

2) The complex formation between the network chains and the linear polymer.

In order to differentiate these two cases, the complex formation within the gel should be examined. IR spectroscopic data (Figure 5.25) of the complex form showed two distinct peaks at about 1600 cm^{-1} and 800-1050 cm^{-1}, the former indicating the valence vibration of pyridine ring and the latter to the asymetric streching of P-O-P peak.

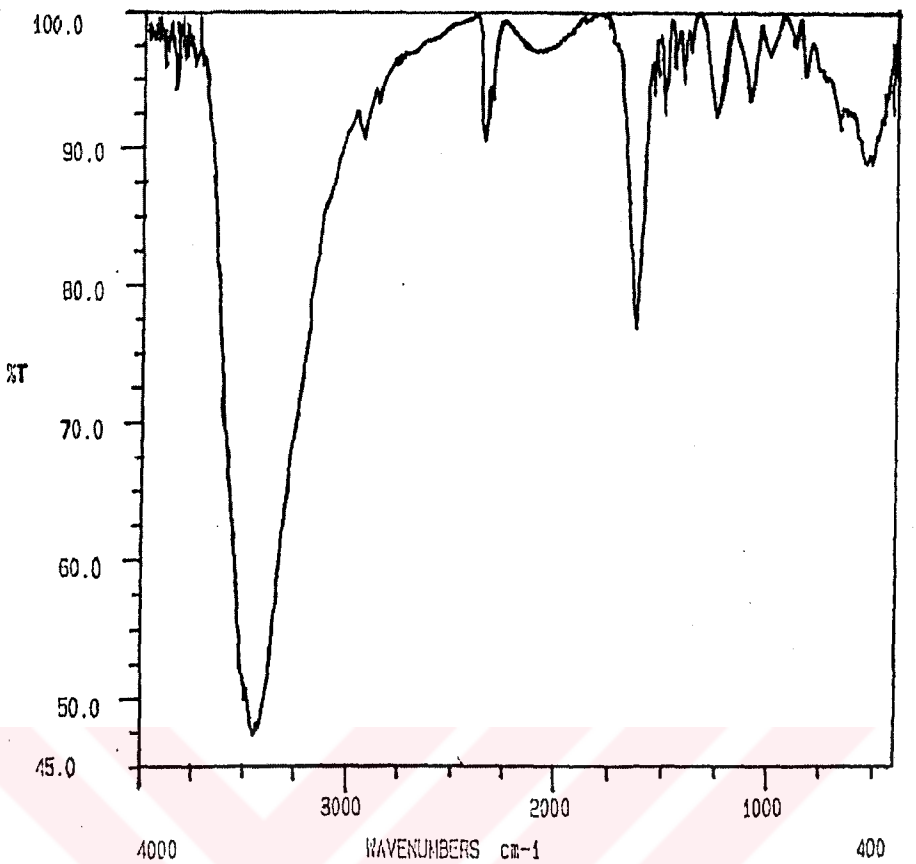


Figure 5.24. IR spectrum of complex of P4VPHCl gel and PSP.

By changing the ionic strength, P4VPHCl gel can undergo a discrete volume phase transition. Increasing NaCl concentration leads to decrease in K_s value.

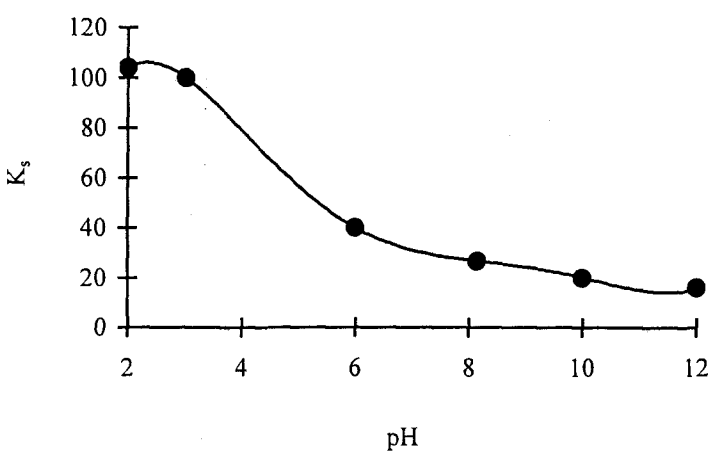


Figure 5.25. Depence of Ks of the complex on pH.

This is more sharply expressed in the region of $0.2 \leq C_{NaCl} < 0.4$ molL^{-1}. P4VPHCl gel is collapsed even in the salt absence through complexation process. Therefore, until $C_{NaCl}=0.2$ molL^{-1} the gel network cannot be influenced by the salt concentration. This phenomenon might be explained with the reformation of complex through the collapse from the uncomplexed parts of the gel. As shown in Figure 5.26 by increasing pH, K_s values decreases.

CHAPTER 6. CONCLUSIONS

The main conclusions drawn from the results and the related discussions can be summarised as follows;

- Insoluble polyelectrolyte complexes were obtained by the interaction of poly (sodiumphosphate)(PSP) with poly(4-vinylpyridiniumchloride)(P4VPHCl) at the given concentration in aqueous solution.

  The stoichiometric ratio of polycation to polyanion was found to be 1:1 as the result of analysis of supernatant liquids in conjunction with the weights of initial polyelectrolytes and the resultant complex.

  The effects of the experimental conditions such as pH, ionic strength and the order of polyion addition on polyelectrolyte complex formation were determined. The electrolyte effect on the PEC (PSP-P4VPHCl) was studied by adding NaCl. The added NaCl was affected the system depending on the concentration in either way; one was the suppression on the complex formation due to excess charges on polyions that caused the regular ionic-crosslink between monomeric units being interrupted, that was, active groups could not come to mutual position, but PEC formation proceeded readily. Secondly, NaCl provided common ion effect on polycation thus it dissociated largely and PEC dissolved. Reaction stoichiometry was independent of the order of addition of polyelectrolyte components of PEC.

  The presence of PEC in dilute aqueous solution was also demonstrated by UV spectroscopy. The time effect on the conformation of PEC was given as a result of turbidity measurements. The results showed that the shape of PEC particles was dependent on the order of addition of polyelectrolyte components of PEC. Initially, PEC particles were rod like in case when PSP was titrant and they

became spherical after a certain period of time whereas spherical conformation of PEC particles did not change with time when P4VPHCl was titrant.

The breakdown of complexes occurred with dissolution reaction at a certain hydrogen ion concentration (10^{-2} M) that corresponds a minimum value using either a strong acid/ base or a weak acid.

DSC measurements of the isolated complexes of PSP-P4VPHCl in different mol ratio displayed well-defined T_g values that were not affected by the order of addition of polyions. Although the observed T_g values was found to be higher than the values given in the literature, the T_g values of any PEC system might be particular according the different properties of the studied system. The decrease in the T_g values of P4VP-PABA complex system compare to T_g value of P4VP suggested that crystalline PABA revealed plasticizing effect on amorphous P4VP.

- Polyelectrolyte complexes were obtained with the reaction poly(sodium phosphate) (PSP) and 4-amino benzoic acid hydrochloride (PABCl) in aqueous solution. The reaction stoichiometry between PSP and PABCl was found to be 1:1.2 as a result of the supernatant analysis and viscosity measurements.The presence of PSP-PABCl complex was also shown in dilute solution by UV spectroscopy; conductometry and viscometry. pH and the ionic strength affected the complex formation. The complete dissolution of the complexes was reached at the salt concentration (NaCl) of 2 M, because of the screening effect of microsalts. PEC formation was suppressed at pH 4.59 .

- Complex formation between poly(4-vinylpyridine) (P4VP) and 4-aminobenzoic acid (PABA) obtained by the evaporation from ethanol solution. Hydrogen bonded P4VP-PABA complex was investigated by IR spectroscopy, DSC, and ^{13}C NMR methods.

  The protonation constants of P4VP-PABA complex in aqueous ethanol solution were calculated as Log K_1=6.45; Log K_2=4.30; Log K_3= 2.38, using Irving-Rossotti method.

Interaction of the transition metal, Cu(II) with P4VP-PABA complex was shown in aqueous ethanol solution potentiometrically and stability constant of complex (PEC-Cu^{2+}) were calculated as $1.59x10^3$ by using Calvin and Melchior method.

- For having the advanced swelling properties of PEC (P4VPHCl-PSP), PSP and P4VP were subjected to radiation for various doses in order to obtain highly crosslinked structures.

  UV spectroscopic studies showed the gelled part of P4VP increased with radiation dose up to 0.61 MGy whereas radiation did not have any affect on PSP. To characterise P4VP gels with respect to their swelling properties to some extend, the crosslinking and chain scission yields were calculated and found to be G_x=0.011 and G_s=$1.56x10^{-3}$, respectively.

  Quaternization of irradiated P4VP sample was achieved using 0.1 M HCl solution to obtain water swellable P4VPHCl gels. The complex reaction between P4VPHCl hydrogel in PSP solution was investigated regarding ionic strength and pH. It was found that the swelling coefficient, K_s, decreased with increasing ionic strength and pH.

REFERENCES

[1] **Michaels, A.S. and Miekka, R.G.,** 1961. Polycation-Polyanion Complexes; Preparation and Properties of Poly(vinylbenzyltrimethyl ammonium) (polystyrene sulfonate), *J. Phys. Chem.*, **65**, 1765-1773.

[2] **Kossel, A.,** 1896. *J. Phys. Chem.*, **22**, 178.

[3] **Tsuchida, E., Osada, Y. and Sanada, K.,** 1972. Interaction of Poly(styrene sulfonate) with Polycations Carrying Charges in the Chain Backbone, *J. Polym. Sci.*, **10**, 3397-3404.

[4] **Kabanov, V.A., Zezin, A.B., Mustafaev, M. and Kasaikin, U.H.,** 1980. Polym. Ammines Ammonium Salts, Pergamon Press Ltd., 173-192.

[5] **Dautzenberg, H., Jaeger, W., Kötz, J., Philipp, B., Seidel, Ch. and Stcherbina, D.,** 1994. Polyelectrolytes, Formation, Characterization and Application, Hanser/Gardner Publication Inc., p.13, Munich.

[6] **Philipp, B., Dautzenberg, H., Kötz, J. and Dawdoff, W.,** 1989. Polyelectrolyte Complexes, Recent Developments and Open Problems, *Prog. Polym. Sci.*, **14**, 91-171.

[7] **Blumstein, A., Kakivaya, S.R. and Salamone, J.C.,** 1974. Matrix Polymerization on an Ionene Template. The Formation of an Ordered Polyelectrolyte Complex, *J. Polym. Sci. Polym. Letters Ed.*, **12**, 651-658.

[8] **Cerrai, P., Guerra, G.D., Tricoli, M., Maltini, S., Barbani, N. and Petarca, L.,** 1996. Polyelectrolyte Complexes Obtained by Radical Polymerization in the Presence of Chitosan, *Macromol. Chem. Phys.*, **197**, 3567-3579.

[9] **Cerrai, P., Guerra, G.D., Maltinti, M., Tricoli, M., Giusti, P., Petarca, L. and Polacca, G.,** 1994. Physicochemical Properties of Poly(allyl ammonium acrylate) Complexes Obtained by Radical Template Polymerization, *Macromol. Rapid. Commun.*, **15**, 983-990.

[10] **Kabanov, V.A., Kargina, O.V. and Ulyanova, M.V.,** 1976. Formation of Crystalline Polyelectrolyte Complexes on Matrix Polymerization, *J. Polym. Sci.*, **14**, 2341-2356.

[11] **Michaels, A.S., Mir, L. and Sahneider, N.S.,** 1965. A Conductometric Study of Polycation-Polyanion Reactions in Dilute Aqueous Solution, *J. Phys. Chem.*, **69**, 1447-1455.

[12] **Domard, A. and Rinaudo, M.,** 1981. Polyelectrolyte Complexes: Interaction Between Poly(L-Lysine) and Polyanions with Various Charge Densities and Degrees of Polymerization, *Macromolecules*, **14**(3), 620-628.

[13] **Tsuchida, E. and Abe, K.,** 1982. Interactions Between Macromolecules in Solution and Intermacromolecular Complexes, *Adv. Polym. Sci.*, **45**, 1-130, Springer-Verlag, New York.

[14] **Dragan, S., Dranca, I., Chimici, L., Cristea, M., Funduionu, G.H. and Lupascu, T.,** 1998. Thermal Behaviour of Some Cationic Polyelectrolyte Complexes, *Eur. Polym.* J., **34**, 733-737.

[15] **Izumrudov, V.A., Zezin, A.B. and Kabanov, V.A.,** 1991. Equilibria in Interpolyelectrolyte Reactions and the Phenomenon of Molecular Recognition in Solutions of Interpolyelectrolyte Complexes, *Russian Chem. Reviews*, **60**(7), 792-806.

[16] **Bekturov, E.S. and Bimendina, L.A.,** 1981. Interpolymer Complexes, *Adv. Polym. Sci.*, **41**, 99-147.

[17] **Tsuchida, E., Osada, Y. and Abe, K.,** 1976. Gel Formation Through Interpolymer Interaction of Poly(methacrylic acid)-Poly(vinylbenzyl trimethyl ammonium chloride), *J. Polym. Sci. Polym. Chem. Ed.*,**14**, 767-771.

[18] **Kalyuzhnaya, I., Rudman, A.R., Vengerova, N.A., Radvodouskii, Y.F., El'tsefon, B.S. and Zezin, A.B.,** 1983. Structure and Properties of Polyelectrolyte Complexes of Poly(acrylic acid) and Polymeric Heterocylic Amines, *Polym. Sci. USSR*, **25**, 2796-2806.

[19] **Kalyuzhnaya, I., Rudman, A.R., Vengerova, N.A., Radvodouskii, Y.F., El'tsefon, B.S. and Zezin A.B.,** 1975. Conditions of Formation and Properties of Membranes, Polyelectrolyte Complexes Prepared Using Weak Polyelectrolytes, **17**, 3201-3209.

[20] **Gulyayeva, ZH.G., Poletayeva, O.A., Kalachev, A.A., Kabanov, V.A. and Zezin, A.B.,** 1976. Study of Water Soluble Polyelectrolyte Complexes Prepared Using Sodium Polyacrylate and 5, 6 Ionene Bromide, *Polym. Sci. USSR*, **18**, 3204-3211.

[21] **Abe, K., Ohno, H. and Tsuchida, E.,** 1977. Phase Changes of Polyion Complex Between Poly(methacrylic acid) and a Polycation Carrying Charges in the Chain Backbone, *Makromol. Chem.*, **178**, 2285-2293.

[22] **Tsuchida, E., Sanada, K. and Moribe, K.,** 1971. Polycation Polymers of the Integral Type Obtained from the Reaction of p-xylenedichloride and tert-diamines, *Makromol. Chem.*, **151**, 207-220.

[23] **Saito, M., Abe, K., Osada, Y. and Tsuchida, E.,** 1974. Ionic Polymers. II. Cooperative Interaction Between Poly(methacrylic acid) and

Poly(ethyleimine) with Different Chain Lengths, *J. Chem. Soc. Japan*, **5**, 977-980.

[24] **Kharenko, O.A., Kharenko, A.V., Kasaiki, V.A., Zezin, A.B. and Kabanov, V.A.**, 1980. Structure of Non-stoichiometric Water Soluble Polyelectrolyte Complexes, *Polym. Sci. USSR*, **21**, 3009-3017.

[25] **Izumrudov, V.A., Kasaikin, V.A., Yermakova, L.N., Zezin, A.B. and Kabanov, V.A.**, 1978. Study of Water Soluble Polyelectrolyte Complexes of Non-equimolar Composition, *Polym. Sci. USSR*, **20**, 452-460.

[26] **Izumrudov, V.A., Zezin, A.B. and Kabanov, V.A.**, 1983. The Formation of Non-stoichiometric Polyelectrolyte Complexes, *Polym. Sci. USSR*, **25**, 2296-2304.

[27] **Kabanov, V.A., Zezin, A.B., Izumrudov, V.A., Bronich, T.K. and Bakeev, K.N.**, 1985. Cooperative Interpolyelectrolyte Reactions, *Macromol. Chem. Suppl.*, **13**, 137-155.

[28] **Kharenko, A.V., Straikova, L. and Zezin, A.B.**, 1976. Study of Cooperative Reactions of Oligo and Polyphosphates with Polybases, *Polym. Sci. USSR*, **18**, 1837-1843.

[29] **Abe, K., Kaide, M. and Tsuchida, E.**, 1977. Complexes of Poly(L-glutamic acid) with Oligo(ethylene imine)'s and Their Quaternary Derivatives: Effect of Chain Length of the Oligomers on Complexation, *Polym. J.*, **9**(1), 73-78.

[30] **Izumrudov, V.A., Kasaikin, V.A., Yermakova, L.N. and Zezin, A.B.**, 1978. Study of Water Soluble Polyelectrolyte Complexes of Non equimolar Composition, *Polym. Sci. USSR*, **20**, 452-460.

[31] **Zhou, X., Goh, S.H., Lee, S.Y. and Tan, K.L.**, 1997. Interpolymer Complexation Between Poly(vinylphosphonic acid) and Poly(vinylpyridines), *Polymer*, **38**, 5333-5338.

[32] **Webster, L., Huglin, M.B. and Robb, I.D.**, 1997. Complex Formation Between Polyelectrolytes in Dilute Aqueous Solution, *Polymer*, **38**, 1373-1380.

[33] **Huglin, M.B., Webster, L. and Robb, I.D.**, 1996. Complex Formation Between Poly(4-vinyl pyridinium chloride) and Poly(sodium-2-acrylamido-2-methyl propane sulfonate) in Dilute Aqueous Solution, *Polymer*, **37**, 1211-1215.

[34] **Fuoss, R.M.**, 1949. Mutual Interaction of Polyelectrolytes, *Science*, **110**, 552-554.

[35] **Rego, J.M., Huglin, M.B. and Gooda, S.R.**, 1990. Potentiometric and Viscometric Studies on Interaction Between Poly(vinyl pyridines) and Acids, *Brit. Polym. J.*, **23**, 333-339.

[36] **Webster, L. and Huglin, M.B.,** 1997. Observations on Complex Formation Between Polyelectrolytes in Dilute Aqueous Solution, *Eur. Polym. J.*, **33**, 1173-1177.

[37] **Kudaibergenov, S.E., Nurkeeva, Z.S., Sigitov, V.B., Azimbekova, K.Zh. and Ushanov, V.Zh.,** 1997. Interpolyelectrolyte Complexes of Poly[4-(but-3-en-1-ynyl)-1-methyl piperidin 4-ol] with Carboxylic acid, *Macromol. Chem. Phys.*, **198**, 183-191.

[38] **Mustafaev, M.I. and Kabanov, V.A.,** 1981. Soluble Ternary Complex of Poly(4-vinylpyridine), Bovin Serum Albumin and Copper, *Polym. Sci. USSR*, **23**, 299-304.

[39] **Subotic, D.V., Ferguson, J. and Warren, B.C.H.,** 1991. Turbidimetric Study of the Influence of Cu^{2+} on the Kinetics of Complexation of Poly(acrylic acid) with Poly(vinylpyrolidone), *Eur. Polym. J.*, **27**, 61-64.

[40] **Boyer, R.F.,** 1963. The Relation of Transition Temperatures to Chemical Structure of High Polymers, *Rubber Chem. Technol.*, **36**(5), 1303-1421.

[41] **Boyer, R.F.,** 1954. Relationship of First to Second Order Transition Temperatures for Crystalline High Polymers, *J. Appl. Phys.*, **25**, 825-829.

[42] **Gibbs, K.R.,** 1956. Nature of the Glass Transition in Polymers, *J. Chem. Phys.* , **25**, 185-186.

[43] **Dunham, K.R., Vanderberghe, J., Faber, J.W.H. and Costois, L.E.,** 1963. Effect of Side Chain Structure on Poly-α-olefin Properties, *J. Polym. Sci. Part A*, **1**, 751-762.

[44] **Rogers, S.S. and Mandelkern, L.,** 1957. Glass Formation in Polymers I. The Glass Transitions of the Poly(n-alkl methacrylates), *J. Phys.Chem.*, **61**, 985-990.

[45] **Barb, W.G.,** 1959. The Effect of Chemical Structure on Softening Points of Substituted Polystyrenes and Related Materials, *J.Polym. Sci.*, **37**, 515-532.

[46] **Glans, J.H. and Turner, D.T.,** 1981. Glass Transition Elevation of Polystyrene by Crosslinks, *Polymer*, **22**, 1540-1543.

[47] **Sasuga, T., Hayakowa, N. and Yoshida, K.,** 1987. Electron Beam Irradiation Effects on Mechanical Relaxation of Aromatic Polysulphones, *Polymer*, **28**, 236-240.

[48] **Seguchi, T., Sasuga, T., Hirade, T. and Hama, Y.,** 1999. Radiation Effects of Aromatic Thermoplastic Polyimide, *Polymer*, **32**, 2499-2504.

[49] **Goh, S.H., Lee, S.Y., Zhou, X. and Tan, K.L.,** 1998. X-Ray Photoelectron Spectroscopic Studies of Interactions Between Poly(4-vinylpyridine) and Poly(styrene sulfonate) Salts, *Macromolecules*, **31**, 4260-4264.

[50] **Cesteros, L.C., Velada, J.L. and Katime, I.,** 1995. Polymer-Polymer Complexation Between Poly(monomethyl itaconate) and Poly(vinylpyridines), *Polymer*, **36**, 3183-3189.

[51] **Itoh, Y., Negishi, K., Iizuka, E., Abe, K. and Kaneko, M.,** 1992. Fluorescence Study of Polyelectrolyte Complex Formation. 2. Effect of Acidity of Polyanions on Complexation, *Polymer*, **33**, 3016-3023.

[52] **Kharenko, O.A., Izumrudov, V.A., Kharenko, A.V., Kasaiki, V.A., Zezin, A.B. and Kabanov, V.A.,** 1980. Association and Dissociation Processes in Solution of Non-stoichiometric Polyelectrolyte Complexes, *Polym. Sci. USSR*, **22**, 247-254.

[53] **Trinh, C.H. and Schnabel, W.,** 1997. Polyelectrolyte Complexes from Poly(N-ethly-4-vinylpyridinium bromide) and Poly(sodium methacrylate). A Stopped-Flow Light Scattering Investigation, *Macromol. Chem. Phys.*, **198**, 1319-1327.

[54] **Izumrudov, V.A., Kharenko, O.A., Kharenko, A.V., Gulyayeva, ZH.G., Kasaiki, V.A., Zezin, A.B. and Kabanov, V.A.,** 1980. Behaviour of Non-Stoichiometric Polyelectrolyte Complexes in Aqueous Salt Solution, *Polym. Sci. USSR*, **22,** 767-776.

[55] **Kabanov, V.A., Mustafaev, M.I. and Goncharov, V.V.,** 1981. Soluble Complexes of Bovine Serum Albumin with Poly(4-vinyl pyridinium) Cations Containing N-cetyl Side Radicals, *Polym. Sci. USSR*, **23,** 287-298.

[56] **Izumrudov, V.A.,** 1996. Polyelectrolyte Complexes and Gels. Competitive Reactions in Solutions of Protein-Polyelectrolyte Complexes, *Ber. Bunsenges. Phys. Chem.*, **100**, 1017-1023.

[57] **Kabanov, V.A.,** 1986. Synthetic Membrane Active Polyelectrolytes in Design of Artificial Immunoges and Vaccines, *Makromol. Chem. Makromol. Symp.*, **104**, 101-124.

[58] **Vishalakshi, B., Ghosh, S. and Kalpagam, V.,** 1993. The Effects of Charge Density and Concentration on the Composition of Polyelectrolyte Complexes, *Polymer,* **34,** 3270-3275.

[59] **Park, S.M., Jean, S.H. and Ree, T.**, 1989. Interpolymer Complex Formation Between Helical Poly(L-proline) and Random-Coil Poly(methacrylic acid) Through Hydrogen Bonding, *J. Polym. Sci. Part A: Polym. Chem.,* **27**, 4109-4117.

[60] **Monal, W.A., Cabrera, G., Peniche, C. and Rinaudo, M.,** 2000. Conductometric Study of the Interpolyelectrolyte Reaction Between Chitosan and Poly(galacturonic acid), *Polymer*, **41**, 2373-2378.

[61] **Park, W.H., Lee, K.Y. and Haa, W.S.**, 1996. Insoluble Polyelectrolyte Complex Formed from Chitosan and α-Keratose Confirmational Change of α-Keratose, *Macromol. Chem. Phys.*, **197**, 2175-2183.

[62] **Ito, H., Shibata, T., Miyamoto, T., Noishiki, Y., and Inagaki, H.**, 1986. Formation of Polyelectrolyte Complexes Between Cellulose Derivatives and Their Blood Compability, *J. Appl. Polym. Sci.*, **31**(8), 2491-2500.

[63] **Ikawa, T., Abe, K., Honda, K., and Tsuchida, E.**, 1975. Interpolymer Complex Between Poly(ethylene oxide) and Poly(carboxylic acid), *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1505-1514.

[64] **Tsuchida, E.**, 1994. Formation of Polyelectrolyte Complexes and Their Structures, *Pure Appl. Chem.*, **A31**(1), 1-15.

[65] **Baranovskii, V.Y., Kazarin, L.A., Litmanovich, A.A., Papisov,I.M. and Kabanov, V.A.**, 1982. Complex Formation Between Poly(methacrylic acid) and Poly(acrylamide), *Polym. Sci. USSR*, **24**, 1683-1688.

[66] **Iliopoulos, I., Halary, J.L. and Audebert, R.**, 1988. Polymer Complexes Stabilized Through Hydrogen Bonds. Influence of Structure Defects on Complex Formation; Viscometry and Fluorescence Polarization Measurements, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 275-284.

[67] **Arguelles-Monal, W., Perez-Gramatges, A., Peniche-Cavas, C., Desbrieres, J. and Rinaudo, M.**, 1998. Conductometric and Viscometric Study of the Macromolecular Complex Between Poly(acrylic acid) and Poly(vinylpyrolidone), *Eur. Polym. J.*, **34**, 809-814.

[68] **Mun, G.A., Nurkeeva, Z.S. and Khutoryanskiy, V.V.**, 1999. Complex Formation Between Poly(vinylether) of Ethylene Glycol and Poly(acrylic acid) in Aqueous and Organic Solutions, *Macromol. Chem. Phys.*, **200**, 2136-2138.

[69] **Fujimori, K., Trainor, G.T. and Costigan, M.J.**, 1984. Complexation and Rate of Polymerization of Acrylic Acid and Methacrylic Acid in the Presence of Poly(4-vinyl pyridine) in Dilute Methanol Solution, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2479-2487.

[70] **Budtova, T.V., Suleimenov, I.E. and Frenkel, S.YA.**, 1994. Interpolymer Complex Formation of Some Nonionogenic Polymers with Linear and Crosslinked Polyacrylic acid, *J. Polym. Sci. Part A: Polym. Chem.*, **32**, 281-284.

[71] **Bimendina, L.A., Bekturov, E.A., Tleubaeva, G.S. and Florova, V.A.**, 1979. Complex Formation Between Poly(vinylpyrolidone) and Poly(itaconic acid mono methyl ester) or Its Copolymer, *J. Polym. Sci. Polym. Symp.*, **66**, 9-14.

[72] **Velada, J.L., Cesteros, L.C. and Katime, I.,** 1996. Interpolymer Association Between Poly(vinylpyridines) and Poly(mono-n-alkyl itaconates). Effect of the n-alkyl Substituent, *Macromol. Chem. Phys.*, **197**, 2247-2259.

[73] **Bimendina, L.A., Roganov, V.V. and Bekturov, E.A.,** 1974. Hydrodynamic Properties of Complexes of Poly(methacrylic acid)-Poly(vinylpyrolidone) in Solutions, *J. Polym. Sci. Polym. Symp.*, **44**, 65-74.

[74] **Staikos, G., Karayanni, K. and Mylonas, Y.,** 1997. Complexation of Polyacrylamide and Poly(N-isopropyl acrylamide) with Polyacrylic acid. The Temperature Effect, *Macromol.Chem. Phys.*, **197**, 2905-2915.

[75] **Deng, S.M. and Li, X.,** 1998. Formation of Polyelectrolyte Complexes Based on Pendant Type Imidazolium Organo Silicon Polymer with Poly(sodium styrene sulfonate), *Polymer*, **39**, 5643-5648.

[76] **Oyama, H.T. and Frank, C.W.,** 1985. Structure of the Polyion Complex Between Poly(sodium p-styrene sulfonate) and Poly(diallyldimethyl ammonium chloride), *J. Polym. Sci. Part B: Polym. Phys.*, **24**, 1813-1821.

[77] **Oyama, H.T. and Nakajima, T.,** 1983. Structure and Sorption Properties of the Polyion Complex Between Poly(acrylic acid) and Poly(4-vinyl pyridine), *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2987-2995.

[78] **Peniche, H., Elvira, C. and Roman, J.S.,** 1998. Interpolymer Complexes of Chitosan and Poly(methyacrylic acid) Derivatives of Salicylic Acid: Preparation, Characterization and Modification by Thermal Treatment, *Polymer*, **39**, 6549-6554.

[79] **Gargallo, L., Gatica, N. and Radic, D.,** 1994. Blends of Poly(monoalkyl itaconates)-Poly(vinylpyridines) and Model Molecules, *Int. J. Polym. Matter*, **27**, 107-115.

[80] **Avramenko, N.V., Kargina, O.V., Prazdnichnaya, O.V., Phrolova, M.N., Jurgens, I.D. and Davidova, S.L.,** 1996. Interpolymer Complexes of a New Type, *J. Therm. Anal.*, **46**, 347-352.

[81] **Izumrudov, V.A., Bronich, T.K., Navikova, M.B., Zezin, A.B. and Kabanov, V.A.,** 1982. Substitution Reactions in Ternary Systems of Macromolecules, *Polym. Sci. USSR*, **24**, 367-378.

[82] **Kabanov, V.A. and Papisov, I.M.,** 1979. Formation of Complexes Between Complementary Synthetic Polymers and Oligomers in Dilute Solution, *Polym. Sci. USSR*, **21**, 261-307.

[83] **Papisov, I.M., Nedyalkova, T.I., Avramchuk, N.K. and Kabanov, V.A.,** 1974. Macromolecular Substitution Reactions and Polymerization in

the Presence of Two Macromolecular Matrices, *Polym. Sci. USSR*, **16**, 2259-2265.

[84] **Izumrudov, V.A., Ortiz, H.O., Zezin, A.B. and Kabanov, V.A.,** 1998. Temperature Controllable Interpolyelectrolyte Substitution Reactions, *Macromol. Chem. Phys.* , **199**, 1057-1062.

[85] **Sato, H., Maeda, M. and Nakajima, A.,** 1979. Mechanochemistry and Permability of Polyelectrolyte Complex. Membranes Composed of Poly(vinyl alcohol) Derivatives, *J. Appl. Polym. Sci.*, **23**, 1759-1767.

[86] **Schwartz, H.H., Richau, K. and Paul, D.,** 1991. Membranes from Polyelectrolyte Complexes, *Polym. Bull.,* **114**, 95-100.

[87] **Vogel, M.K., Cross, R.A., Bixler, H.J. and Guzman, R.J.,** 1970. Medical Uses for Polyelectrolyte Complexes, *J. Macromol. Sci. Chem.*, **73**, 675-692.

[88] **Seki, K. and Tirrell, D.A.,** 1984. pH Dependent Complexation of Poly(acrylic acid) Derivatives with Phospholipid Membranes, *Macromolecules*, **17**, 1692-1698.

[89] **Deasy, P.B.,** 1984. Microencapsulation and Related Drug Process, Marcel Dekker, Basel.

[90] **Refojo, M.F.,** 1967. Polyelectrolyte Complexes: Permability to Water and Potential Uses in Ophthalmology, *J.Appl. Polym.Sci.*, **11**, 1991-2000.

[91] **Mark, H.F., Bilakes, N.M., Overberger, C.G., Menges, G. and Kroschwitz, J.I.,** 1988. Encyclopedia of Polymer Science and Engineering, Vol.11, John Wiley & Sons Inc., New York, 720-739.

[92] **Reilly Report**, 1989. Linear Polyvinylpyridines, Properties and Applications, Reilly Industries Inc., Indianapolis.

[93] **Strauss, U.P., Smith, E.H. and Wineman, P.L.,** 1953. Polyphosphates as Polyelectrolytes. I. Light Scattering and Viscosity of Poly(sodium phosphate) in Electrolyte Solutions, *J. Am. Chem.Soc.*, **75**, 3935-3940.

[94] **Salamone, J.C.,** 1996. Polymeric Materials Encyclopedia, Vol.27, 5090-5091.

[95] **Bekturov, E.A. and Bakuova, Z.Kh.,** 1986. Synthetic Water Soluble Polymers in Solution, p.55, Hüthing & Wepf Verlag, New York.

[96] **Hunter, D.N.,** 1963. Inorganic Polymers, p.66, Blackwell Scientific Publications, London.

[97] **Ray, N.H.**, 1978. Inorganic Polymers, p.30, Academic Press, London.

[98] **Van Wazer, J.R.**, 1958. Phosphorus and Its Compounds, Vol.1, p.454, Interscience, New York..

[99] **Dole, M.,** 1986. History of Olefins, (Seymour, R.B., Cheng, T., Eds.), p.71, Reidel, Boston.

[100] **Little, K.,** 1952. Irradiation of Linear High Polymers, *Nature*, **170**, 1075-1076.

[101] **Brown, J.R. and O'Donnell, J.H.,** 1979. Effects of Gamma Radiation on Two Aromatic Polysulfones. II. A Comparison of Irradiation at Various Temperatures in Air-Vacuum Environments, *J. Appl. Polym. Sci.*, **23**, 2763-2775.

[102] **Lawton, E.J., Bueche, A.M. and Balwit, J.S.**, 1953. Irradiation of Polymers by High Energy Electrons, *Nature*, **172**, 76-77.

[103] **Kells, D.I.C., Koike, M. and Guillet, J.E.,** 1968. Direct Determination of Crosslinking and Chain Scission in Polymers, *J. Polym. Sci. Part A: Polym. Chem. Ed.*, **6**, 595-601.

[104] **Nichol, J.M., O'Donnell, J.H., Rahman, N.P. and Winzor, D.J.,** 1977. Evaluation of Crosslinking and Scission Yields in the Degradation of Polystyrene by γ-Irradiation in Air, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 2919-2933.

[105] **O'Donnell, J.H., Rahman, N.P. and Smith, C.A.,** 1979. Crosslinking and Scission Yields for Polystyrene Subjected to γ-Irradiation in Vacuo, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 4081-4088.

[106] **Brown, J.R. and O'Donnell, J.H.,** 1975. Effects on Gamma Radiation on Two Aromatic Polysulfones, *J. Appl. Polym. Sci.*, **19**, 405-417.

[107] **Brown, J.R. and O'Donnell, J.H.,** 1970. The Radiation Stability of an Aromatic Polysulfone, *J.Polym.Sci. Polym. Letters*, **8**, 121-126.

[108] **Graessley, W.W.,** 1964. The Measurement of Molecular Weight Distribution in Polymers by Crosslinking-Solubility Methods, *J.Phys. Chem.*, **68**, 2258-2263.

[109] **Parkinson, W.W. Bopp, C.D., Binder, D. and White, J.E.,** 1965. A Comparison of Fast Neutron and γ-Irradiation of Polystyrene, *J.Phys. Chem.*, **69**, 828-833.

[110] **Sasuga, T., Hayakawa, N., Yoshida, K. and Hagiwara, N.,** 1985. Molecular Motion of Non-crystalline Poly(acryl ether-ether-ketone) (PEEK) and Influence of Electron Beam Irradiation, *Polymer*, **26**, 1039-1045.

[111] **Taylor, A.G. and Harmon, J.P.,** 1993. Structure and Dose Rate Effects on Optical Radiation Hardness in Scintillator Polymer, *Radiat. Phys. Chem.*, **41**, 115-119.

[112] **Mateev, M., Karageorgiev, S. and Atanasova, B.,** 1996. Gel-Sol Analysis of the Effect of Electron Beam Irradiation on the Macromolecular

Structure and Crosslinking Parameters in Low Density Polyethylene Films, *Radiat. Phys. Chem.*, **48**, 437-442.

[113] **Sevil, U.A. and Güven, O.,** 1995. Spectroscopic, Viscometric and Mechanical Characterization of γ-Irradiated Isotactic Polypropylene Syringes, *Radiat. Phys. Chem.*,**46**, 875-878.

[114] **Bhateja, S.K. and Young, R.J.,** 1983. Radiation-Induced Crystallinity Changes in Linear Polyethylene, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 523-536.

[115] **Matsuo, H. and Dole, M.,** 1959. Irradiation of Polyethylene (IV). Oxidation Effect, *J. Phys.Chem.*, **63**, 837-843.

[116] **Bowner, T.N., O'Donnell, J.H. and Winzor, D.J.,** 1981. Irradiation of Aromatic Polymers: The Effect of Irradiation Temperature on Crosslinking and Scission in Polystyrene, *J. Polym. Sci. Polym. Chem. Ed.*, **19,** 1167-1174.

[117] **Güven, O. and Şen, M.,** 1991. Preparation and Characteriation of Poly(n-vinyl-2-pyrolidone) Hydrogels, *Polymer*, **32**, 2491-2495.

[118] **Huglin, M.B. and Zakaria, M.B.,** 1986. Swelling Properties of Copolymeric Hydrogels Prepared by Gamma Irradiation, *J.Appl. Polym. Sci.*, **31**, 457-475.

[119] **Clegg, D.W.,** 1991. Irradiation Effects on Polymers, p.60, Elsevier Science Publisher, London.

[120] **Lyson, A.M., Vasile, M.J., Pearce, E.M. and Waszczak, J.V.,** 1988. Copper Chloride Complexes with Poly(2-vinylpyridine): Preparation and Redox Properties, *Macromolecules*, **21**, 3125-3134.

[121] **Bekturganova, G.K., Dzhumadilov, T.K. and Bekturov, E.A.,** 1996. Electroconductivity and Viscosity of Complexes of Poly(vinyl pyridines) with Alkali Metal Salt in Organic Solvents, *Macromol. Chem. Phys.*, **197**, 105-111.

[122] **Berkowitz, J.B., Yamin, B. and Fuoss, R.M.,** 1958. The Flory Constants for Poly(4-vinylpyridine) in Ethanol, *J.Polym. Sci.*, **28**, 69-81.

[123] **Kolthoff, I.M. and Sandel, E.B.,** 1950. Textbook of Quantitative Inorganic Analysis, MacMillan, London, ch.17.

[124] **Strauss, U.P. and Wineman, P.L.,** 1958. Molecular Dimensions and Interactions of Long Chain Polyphosphates in Sodium Bromide Solution, *J. Am. Chem. Soc.*, **80**, 2366-2371.

[125] **Furman, N.H.,** 1962. Standard Methods of Chemical Analysis, NJ: Van Nostrand, Princeton, 832.

[126] **Bernhart, D.N. and Wreath, A.R.,** 1955. Colorimetric Determination of Phosphorus by Modified Phosphomolybdate Method, *J. Anal. Chem.*, **27**, 440-441.

[127] **Jeffery, G.H., Bassett, J., Mendham, J. and Denney, R.C.**, 1989. Vogel's Textbook of Quantitative Chemical Analysis, Wiley-Interscience, New York.

[128] **Mussini, T., Cosvington, A.K., Longhi, P. and Rondinini, S.**, 1985. Criteria for standardisation of pH Measurements in Organic Solvents and Water+Organic Solvent Mixtures of Moderate to High Permittivities, *Pure & Appl. Chem.*, **57** (6), 865-876.

[129] **Champbell, D. and White, J.R.,** 1989. Polymer Characterization (Physical Techniques), Chapman & Hall, London, ch.4, 48-49.

[130] **Baysal, B., Okay, O. and Kayaman, N.,** 1997. Phase Transition of Polyacrylamide Gels in PEG Solutions, *Polym. Gels & Network*, **5**, 167-184.

[131] **Şen, M., Yakar, A. and Güven, O.,** 1999. Determination of Average Molecular Weights Between Crosslinks from Swelling Behaviours of Diprotic acid-Containing Hydrogels, *Polymer*, **40**, 2969-2974.

[132] **Eisenberg, A., Farb, H. and Cool, L.G.,** 1996. Glass Transitions in Ionic Polymers, *J. Polym. Sci. Part A-2*, **4**, 855-868.

[133] **Dragan, S., Cristea, M., Luca, C. and Siminescu, B.C.**, 1996. Polyelectrolyte Complexes. I. Synthesis and Characterization of Some Insoluble Polyanion-Polycation Complexes, *J. Polym. Sci. Polym. Chem.*, **34**, 3485-3494.

[134] **Lysaght, M.J.**, 1975. Ionic Polymers, Applied Science Publishers, London.

[135] **Acar, N.,** 1994. M.S. Thesis, Technical University of Istanbul.

[136] **Ohno, H., Abe, K. and Tsuchida, E.,** 1978. Solvent Effect on the Formation of Poly(methacrylic acid)-Poly(N-vinyl-2-pyrolidone) Complex Through Hydrogen Bonding, *Makromol. Chem.*, **179,** 755-763.

[137] **Johson, S.L. and Ruman, K.A.,** 1965. Infrared Spectra of Solid 1:1 Pyridine-Benzoic Acid Complexes; The Nature of the Hydrogen Bond as a Function of the Acid – Base Levels in the Complex, *J. Phys. Chem.*, **69**, 74-86.

[138] **Odinokov, S.E., Marshkovsky, A.A., Glazunov, V.P., Fogansen, A.V. and Rassadin, B.V.,** 1972. Spectral Manifestations of Intermolecular and Interionic Hydrogen Bonding in Adducts of Various Acids with Pyridine, *Spectrochim Acta*, **32**(A), 1355-1363.

[139] **Kato, T., Kihara, H., Uryu, T., Fujishima, A. and Frechet, J.M.S.,** 1992. Molecular Self-Assembly of Liquid Crystalline Side-Chain Polymers

Through Intermolecular Hydrogen Bonding. Polymeric Complexes Built from a Polyacrylate and Stilbazoles, *Macromolecules*, **25**, 6836-6841.

[140] **Irwing, H.M. and Rossotti, H.S.,** 1954. Complexes from pH Titration Curves in Mixed Solvents, *J. Am. Chem. Soc.*, **76,** 2904-2917.

[141] **Inczedy, J.,** 1980. Analytical Applications of Complex Equilibria, John Wiley-Sons Inc., New York, p.90.

[142] **Hegazy, E.A., Dessouki, A.M., Rabie, A.M. and Ishigaki, I.,** 1984. Membranes Obtained by Preirradiation Grafting of Acrylic Acid onto Poly(tetrafluoroethylene- Perfluoro vinyl ether), *J.Polym. Sci. Polym.Chem. Ed.*, **22**, 3673-3685.

[143] **Hegazy, E.A., Ishigaki, I. and Okamoto, J.,** 1981. Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. I. Kinetic Study of Preirradiation Grafting onto Poly(tetra fluoro ethylene), *J. Appl. Polym. Sci.*, **26**, 3117-3124.

[144] **Charlesby, A. and Pinner, S.H.,** 1959. Analysis of the Solubility Behaviour of Irradiated Polyethylene and other Polymers, *Proc. Royal. Soc.* (London), **A249**, 367-386.

[145] **Charlesby, A.,** 1960. Atomic Radiation and Polymer, Pergamon Press Inc., New York, p.172.

[146] **Shimizu, Y. and Mitsui, H.**, 1979. Gamma Irradiation Induced Crosslinking of Polystyrene, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2307-2316.

[147] **Hegazy, E.A., Abdel-Maksoud, A., Osman, M.B.S. and Mostafa, A.B.,** 1995. Preparation and Thermal Characterization of Graft Copolymer Obtained by Radiation Grafting of Individual and Binary Monomer Systems, *Polym. Int.*, **36**, 47-56.

[148] **Peppas, N.A.,** 1991. Physiologically Responsive Hydrogels, *J. Bioact. Compat. Polym.*, **6**, 241-246.

[149] **Peppas, N.A. and Klier, J.,** 1991. Structure and Swelling Behaviour of Polyethylene Glycol/Poly(methacrylic acid) Complexes, *Stud. Polym. Sci.*, **8** (Absorbent Polym. Technol.), 147-169.

[150] **Philippova, O.E., Karybiants, N.S., Starodoubtsev, S.G. and Khokhlov, A.R.,** 1996. Conformational Transitions in Poly(methacrylic acid) Gel/Poly(ethylene glycol) Complexes. Effect of the Gel Cross-linking Density, *Macromol. Chem. Phys.*, **197**, 2373-2378.

[151] **Flory, P.J. and Rehner, J.**, 1943. Statistical Mechanics of Crosslinked Polymer Networks. I. Rubberlike Elasticity, *J. Chem. Phys.*, **11**, 512-520.

[152] **Flory, P.J. and Rehner, J.,** 1943. Statistical Mechanics of Crosslinked Polymer Networks. II. Swelling, *J. Chem. Phys.,* **11,** 521-526.

[153] **Flory, P.J.,** 1953. Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York.

[154] **Charlesby, A.,** 1953. Swelling Properties of Polystyrene Crosslinked by High Energy Radiation, *J. Polym. Sci.*, **11**, 521-529.

[155] **Bekturov, E.A., Frolova, V.A. and Bimendina, L.A.,** 1999. Swelling Behaviour of a Non-ionic Poly(N-vinyl-2-pyrolidone) Gel in a Linear Poly(acrylic acid) Solution, *Macromol. Chem. Phys.*, **200**, 431-435.

CURRICULUM VITAE

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