

Photopolymerization of Acrylonitrile in Concentrated Aqueous Zinc Halide Solutions

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ABSTRACT: Crosslinked polyacrylonitrile (PAN) was obtained with a high yield from the photoinduced polymerization of acrylonitrile (AN) in concentrated aqueous zinc chloride solution. It was found that the presence of zinc chloride results in the promotion of the radical generation in the photoinitiation process as well as an increase in the rate of propagation. Any attempt to isolate the polymer from the reaction mixture was not successful due to the insolubility of the polymer to any conventional solvents to polyacrylonitrile (PAN); therefore, the reaction mixtures, consisting of PAN, zinc chloride, and water—which are referred to as the polymer hybrid system—was used without further purification. The effect of other zinc halides on the polymerization such as zinc bromide and zinc iodide was also investigated in connection with the photoinitiation mechanism, which reveals that the complex $(Zn^{++}(AN)_x(OH^-)_yCl_{4-(x+y)}^-)$ is the species that is responsible for the photoinitiation. It was found that the transparent, stretchable polymer hybrid systems are electric conductive and turn to black upon heating to 160°C due to the conversion of the nitrile group of PAN to tetrahydronaphthridine rings. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2588–2594, 2000

Key words: photoinitiation; complex; polymer hybrid system; electric-conductive; tetrahydronaphthridine

INTRODUCTION

It has been known that the radical polymerization of some vinyl monomers having polar pendant groups are remarkably enhanced in the presence of some metal halides. The polymerization of acrylonitrile (AN) or methylmethacrylate, initiated by conventional radical initiator, is drastically accelerated in the presence of $LiCl^1$ or $ZnCl_2$.² The acceleration effect of zinc chloride was also observed in the radiation-induced polymerization of AN, and it was concluded that the acceleration effect of zinc chloride was attributed to the increased rate of propagation due to the complex formation of AN with zinc chloride.^{3–5}

It was found that crosslinked polyacrylonitrile (PAN) is obtained from the photo-induced polymerization of AN in concentrated aqueous zinc chloride solution with a high yield in the absence of any initiator. In this article, we report the results of photoinduced polymerization of AN in the concentrated aqueous solutions of zinc halides such as zinc chloride, zinc bromide, and zinc iodide.

EXPERIMENTALS

Materials

AN of reagent grade (Janssen Chemical Co.) was purified by fractional distillation after successive washing with 5% aqueous sodium hydroxide solution, sulfuric acid, 20% aqueous sodium bicarbonate solution, and distilled water, and drying

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over a molecular sieve. Reagent grade *N,N*-dimethylformamide (DMF), zinc chloride (Shinyo Pure Chemical Co.), zinc bromide (Aldrich), and zinc iodide (Aldrich) were used as received.

Photoinduced Polymerization

Various ternary systems, consisting of AN–ZnCl₂–H₂O, in a Pyrex ampoule, were degassed on a high vacuum line by a repeated freeze–thaw method, and then sealed off. The ampoules were placed in a Dewar bottle filled with an ice–water mixture. A 500-W high-pressure Hg lamp (Ushio UI-501-C, Japan) was used as a light source. No filter was used in irradiation. After irradiation, the ampoule was opened and poured into excess methanol or water. The percent conversion was determined by gravimetry.

Analysis

A Nicolet 520p FTIR spectrometer was used for the IR measurement of the monomer ternary systems, consisting of ZnCl₂–AN–H₂O and the polymer mixture systems, consisting of ZnCl₂–PAN–H₂O. A cell, composed of two pieces of a CaF₂ window and a lead spacer of proper thickness, was used for the liquid monomer ternary systems and a thin film of the hybrid polymer system prepared by stretching were used for IR measurements. The electric conductivity of the hybrid polymer systems of thin film sandwiched by Al foils were measured by a two probe method using a constantan voltage source.

Thermal Behaviors

The thermal behaviors of the hybrid polymer ternary systems, consisting of PAN, zinc chloride, and water, were examined by Shimadzu DSC-50 in the temperature range from 50 to 300°C at a rate of 10°C/min, using α -alumina as a reference.

RESULTS AND DISCUSSION

Figure 1 shows the time–conversion curves of photo-induced polymerization of AN in concentrated aqueous zinc chloride solution at 25°C. The comparison of curves 1 and 5 reveals that the polymerization of AN is drastically enhanced in the presence of zinc chloride. Actually, no polymer was obtained in the absence of zinc chloride. The acceleration of the polymerization is mostly significant in a 1 : 1 : 2 system (curve 1) and the least

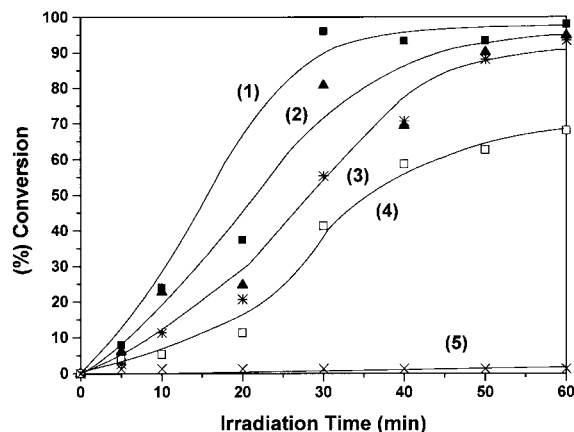


Figure 1 Time–conversion curves of AN in concentrated aqueous zinc chloride solution at 25°C. Compositions of the monomer ternary systems are expressed in a molar ratio of ZnCl₂ : AN : H₂O (1) 1 : 1 : 2, (2) 1 : 2 : 2, (3) 1 : 2 : 3, (4) 1 : 2 : 5, (5) 0 : 1 : 0.18.

in a 1 : 2 : 5 (curve 4) when the composition of the ternary system is expressed in the molar ratio of ZnCl₂, AN, and H₂O. The conversion to polymer in a 1 : 1 : 2 system, containing the highest ZnCl₂ content, reaches almost 100% within 30 min irradiation at 25°C; however, the conversion of the 1 : 2 : 5 system, containing the lowest ZnCl₂ content, shows a value less than 70% even though the irradiation is continued for 60 min at 25°C. The polymerization of the other ternary systems, having different compositions from those shown in Figure 1, has not been carried out because the homogeneity of the monomer ternary system is kept within a very narrow range of the composition.³

Summarizing the results mentioned above, it is evident that the polymerization is sensitively dependent on the composition of the ternary system. Namely, the higher the mol fraction of ZnCl₂ of the ternary system, the higher the rate of polymerization; on the contrary, the rate of polymerization decreases as the mol fractions of the components other than ZnCl₂ increase.

Figure 2 shows some IR spectra of the monomer ternary systems. The absorption band at around 2240 cm⁻¹ due to the stretching vibration of nitrile group is shifted to 2270 cm⁻¹ by the formation of σ -type complex with zinc chloride via a lone-pair electron of the nitrogen atom.³ The coexistence of the two absorption bands indicates that equilibrium is established between the free nitrile and complexed nitrile group in the monomer ternary systems, and the ratio of the nitrile

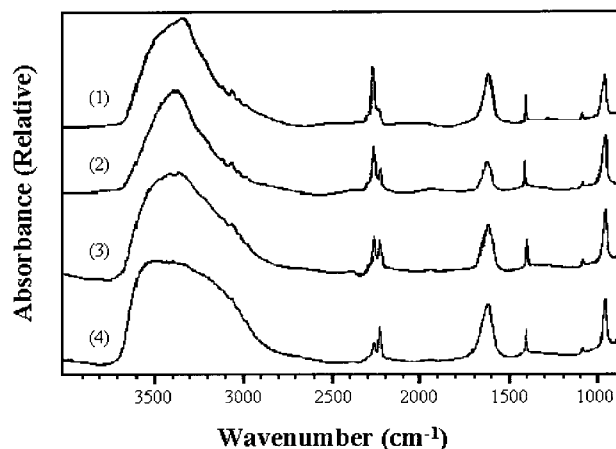


Figure 2 IR spectra of the monomer ternary systems, consisting of ZnCl_2 , AN, and H_2O . Compositions of the systems are same as those given in Figure 1. (1) 1 : 1 : 2, (2) 1 : 2 : 2, (3) 1 : 2 : 3, (4) 1 : 2 : 5.

group in the free and complexed state is sensitively affected by the composition of the system. Therefore, it is believed that the absorbance ratio of D_{2270}/D_{2240} gives an information on the ratio of the concentration of AN in the complexed and free state. The decreasing tendency of D_{2270}/D_{2240} with the increasing mol fractions of H_2O and AN of the ternary system, implies that AN and H_2O competes with each other for the ligand site of zinc ion in this system. The concentration

of AN in the complexed state in the system decreases as the ligand site of zinc ion is occupied by a water molecule; thus, $[\text{Zn}^{++}\text{-AN}]/[\text{AN}]$ decreases as $[\text{AN}]/[\text{ZnCl}_2]$ increases when the mol fraction of water of the system is kept constant. This reveals that the acceleration of the polymerization of AN in the presence of zinc chloride is ascribed to the complex formation of AN with zinc ion, and the acceleration becomes more significant as the concentration of the AN–zinc ion complex in the monomer ternary system increases.

Because it was found that the pH values of the monomer ternary systems are acidic, and the pH value decreases as the concentration of zinc chloride of the monomer ternary system increases, the effect of pH on the polymerization of AN in the monomer ternary system was investigated. The results are summarized in Table I. Although the effect of proton on the polymerization is not as significant, the results clearly show that polymerization is decelerated by the addition of a proton, and vice versa when a hydroxyl ion is added. It is postulated that the pH values of the systems are not greatly affected by the addition of the proton because the pH value of the original monomer ternary systems are highly acidic. Three ligand species, i.e., water, monomer, and chloride ion, coexist in this monomer ternary system and compete with each other for the ligand sites of zinc ion. Acidity of the monomer ternary system is

Table I Additive Effect on the Photo-Initiated Polymerization of AN in Concentrated Aqueous Solution

Zinc Halide	Compositions in Mol Ratio of			Other Additive in Mol Ratio to ZnX_2	pH	Conversion (%)
	ZnX_2 :	AN :	H_2O			
ZnCl_2	1	2	2	None	1.88	100
	1	1	2	None	1.40	100
	1	0.5	3	None	2.12	73.2
	1	0.5	6	None	2.62	10.5
	1	0.5	30	None	6.80	Trace
	1	0.5	6	HCl 0.53	0 ^a	10.8
	1	0.5	6	HBr 0.53	0 ^a	8.4
	1	0.5	6	NaOH 0.09	3.17	14.2
	1	0.5	6	Na_2CO_3 0.09	3.15	21.1
ZnBr_2	1	0.5	3	None	1.04	27.81
	1	0.5	6	None	1.44	0
	1	0.5	6	HCl 0.67	0 ^a	0
ZnI_2	1	0.5	6	HBr 0.67	0 ^a	0
	1	0.5	6	None	2.6	0

Photoirradiated for 60 min at 0°C for degassed samples.

^a Negative values in pH measurement.

explainable when we consider a release of the proton from the water molecule coordinated to the zinc ion [eq. (1)]. The dependence of the polymerization on pH gives evidence that the process of radical production in the photoinitiation of the monomer ternary system is closely related to the presence of the hydroxyl ion-coordinated zinc ion.

It is also evident that polymerization of AN is greatly depressed in the water-rich system due to the dissociation of the AN–zinc ion complex [eq. (1)]. This indicates the possibility that the AN–zinc ion complex plays a certain role in the production of radical species in the photoinitiation process besides playing a role in the enhancement of the propagation. Also, it has been reported that when the radiation-induced polymerization of AN in dilute aqueous zinc chloride solution is remarkably enhanced, even the mol fraction of H₂O is very high.⁵

Furthermore, it becomes clear that the rate of polymerization is also dependent on the halide ion of the zinc salt used, indicating that the efficiency of radical production in the photoinitiation process is affected by the halide ion. The chloride ion is the most effective, and iodide ion is the least in the production of radical species in photoinitiation. Actually, no polymer was obtained from the system, consisting of zinc iodide, AN, and water. It has been reported that zinc ion in an aqueous solution of zinc chloride exists as a chloro–zinc ion complex, presumably in a di- or trichloro complex.^{6–13} Chloride ion competes for the ligand site of zinc ion with other bases such as water or a monomer. As a consequence, the concentration of the chloro–zinc ion complex decreases as the water content increases in the aqueous zinc chloride solution increases³ [eq. (1)]. This also implies the possibility that the chloro–zinc–ion complex plays in certain role in the production of radical species in the photoinitiation process, and the efficiency of the photoinitiation is determined by the halide ion coordinated to the zinc ion. This was supported by the fact that no polymer results from the water-rich monomer ternary system where the concentrations of both complex of zinc ion with AN and chloride ion are low due to the shift of the equilibrium toward the direction of the dissociation.

It was found that no polymer was obtained from the photoinduced polymerization of the monomer ternary system, which was carried out at –78°C, as shown in Table II. This is strikingly different from that observed in radiation-induced polymerization. In radiation-induced polymeriza-

Table II Comparison of the Results of the Polymerization in the Monomer Ternary Systems, Carried Out at 25 and –78°C

Reaction Temperature (°C)	Conversion (%)
25	100
–78	0

Photoirradiated for 60 min.

Composition, expresses in molar ratio of ZnCl₂ : AN : H₂O = 1 : 2 : 2.

tion a higher rate of polymerization was observed at –78°C than that carried out at 0°C.⁴ It was concluded that the enhancement effect of zinc chloride in the radiation-induced polymerization of AN was ascribed to the complex formation of AN with the zinc ion, whose propagating reactivity is much higher than that of the monomer in the free state. It has been reported that the higher rate of polymerization at the lower temperature when compared to that carried out at higher temperature range was reasonably explained by the increased concentration of the AN–zinc ion complex.

The fact that no polymer is obtained at the low temperature range in the photoinduced polymerization strongly suggests that the chloro–zinc ion complex plays a decisive role in the generation of the radical species in the photoinitiation process. If the process of generation radical species is operative, the rate of polymerization at –78°C should be much higher than that carried out at 0°C, as was observed in the corresponding radiation-induced polymerization systems.⁴ It has been known that the stability of the chloro–zinc ion complex also increases as the temperature is lowered, due to the exothermic nature of the complex formation; however, chloride ion of the complex is preferentially replaced by AN³ at the low temperature range. Because the complex formation of AN with zinc ion is more exothermic than that of the chloro–zinc ion complex, as a consequence, concentration of the chloro–zinc ion complex³ decreases with temperature lowering [eq. (2)].

Thus, it is concluded that the tetrahedral zinc ion,⁵ coordinated with AN, hydroxyl ion, and chloride ion, (Zn⁺⁺(AN)_x(OH[–])_yCl_{4–(x+y)}[–]), where the values of *x* and *y* are not larger than 2, plays dual roles in the photoinduced polymerization of AN, not only in the increase in the rate of propagation but also in the radical production in the photoinitiation process [eq. (3)].

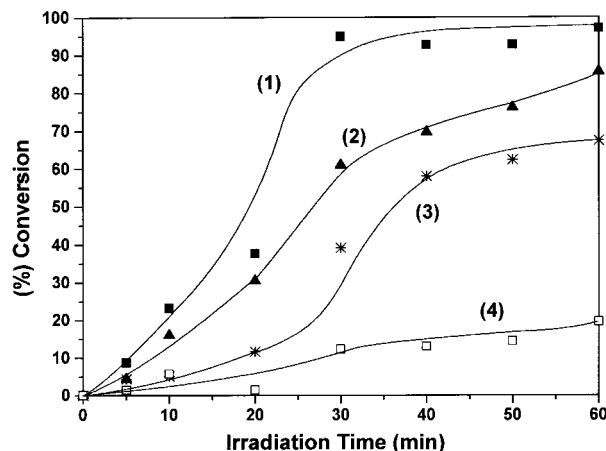
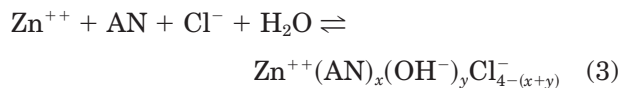
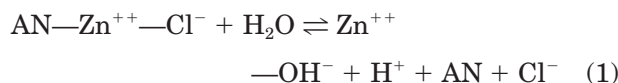


Figure 3 Time-conversion curves of AN in concentrated aqueous zinc chloride solution at 25°C in the absence and presence of oxygen. Compositions of the monomer ternary systems are expressed in a molar ratio of ZnCl_2 : AN : H_2O . (1) 1 : 1 : 2 in the absence of oxygen, (2) 1 : 1 : 2 in the presence of oxygen, (3) 1 : 2 : 3 in the absence of oxygen, (4) 1 : 2 : 3 in the presence of oxygen.



The polymerization in this system is believed to be initiated by the UV or visible rays having wavelengths above 300 nm, because Pyrex ampoules were used as reaction vessels; however, no particular absorption band above 300 nm was observed in a UV spectrum of the monomer ternary system. It was found that the polymerization proceeds by diffusive light in the system, although the rate of polymerization is very low. When the ampoule containing the monomer ternary system is placed in the laboratory at room temperature, a polymer is obtained with a high yield, a polymer that is not soluble to any conventional solvent of PAN due to a crosslinked structure, which is essentially the same as that obtained under photoirradiation with a high-pressure Hg lamp. Any attempt to isolate the polymer from the ternary system was not successful, due to its insolubility to any conventional solvent to PAN such as DMF or dimethylsulfoxide. The re-

action mixtures, which consist of ZnCl_2 , PAN, and H_2O , is, therefore, referred to as a hybrid polymer system in this article.

Figure 3 shows the effect of oxygen on the photoinduced polymerization of the monomer ternary system. It is obvious that the polymerization is retarded in the presence of oxygen, a radical scavenger. This gives evidence of the radical nature of the active species of this polymerization; however, the retardation effect of oxygen on the polymerization is not as significant. The polymerization is not completely inhibited in the presence of oxygen. It is well known that radical polymerization of AN in bulk or solution is inhibited by oxygen, a radical scavenger. It is obvious that the retardation effect of oxygen in the 1 : 2 : 3 is more significant than that observed in the 1 : 1 : 2 system. The ineffectiveness of oxygen in scavenging the radical polymerization is explainable when we consider the retardation of diffusion of oxygen in the medium of the monomer ternary system having high viscosity, and the viscosity of the system increases as the mol fraction of zinc chloride increases. Accordingly, the more significant retardation effect of oxygen is observed in the less viscous system having a composition of 1 : 2 : 3.

Figure 4 shows some DSC curves of the hybrid polymer systems, which consist of polymer, zinc chloride, and water. As mentioned earlier, the polymer obtained from the ternary monomer system is insoluble with any conventional solvents for PAN, which reveals the simultaneous operation of the crosslinking process with the vinyl

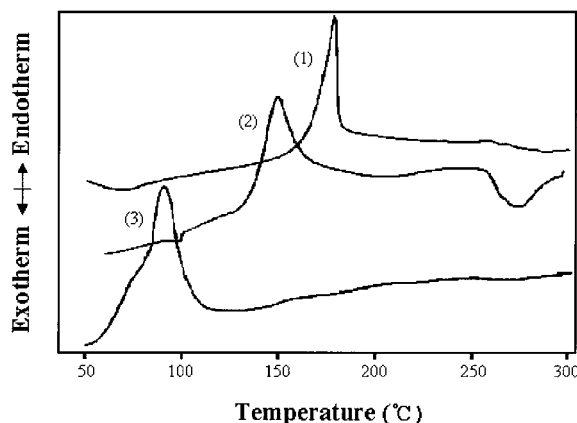


Figure 4 DSC curves of the various hybrid polymer systems, consisting of ZnCl_2 , PAN (as AN base) and H_2O . Compositions of the systems are expressed same as those given in Figure 1. (1) 1 : 1 : 2, (2) 1 : 2 : 2, (3) 1 : 2 : 3.

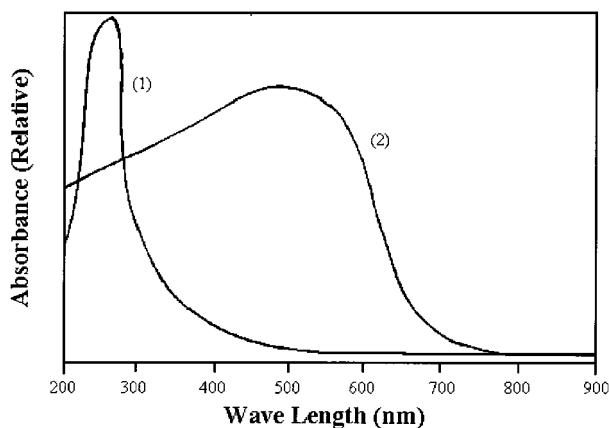


Figure 5 UV spectra of the hybrid polymer film, consisting of ZnCl_2 , PAN, and H_2O . Composition of the system is expressed in a molar ratio of ZnCl_2 : PAN (as AN base) : H_2O = 1 : 1 : 2. (1) Before heat treatment, (2) after heating to 170°C .

polymerization. The hybrid polymer systems having the shape of a circular bar, whose shape is the same as that of the ampoule, are transparent, flexible, and stretchable at room temperature.

Furthermore, dramatic color change appears when heated to 140°C . When the hybrid polymer system of 1 : 1 : 2 is heated, the system is yellow, colored at about 140°C , and the color is changed to black at about 170°C . Figure 5 shows UV spectra of hybrid polymer films, prepared by a simple stretching of the reaction mixture. The absorption maximum at 220 nm at room temperature is gradually shifted to 500 nm by heating to 160°C . This suggests that the exothermic peak appearing in the DSC curves in the range of 60 – 180°C seems to be closely related with the color appearance of the hybrid polymer system.

The formation of the chromophore unit in the hybrid polymer system has been investigated by means of IR spectroscopy. Figure 6 shows IR spectra of the polymer hybrid system having a composition of 1 : 1 : 2. The simultaneous decrease in absorption peaks at 2270 and 2240 cm^{-1} due to the nitrile group in the complexed and free state and increase in the absorption band around 1600 cm^{-1} upon heating reveals that the nitrile group of the polymer hybrid system is converted to $\text{C}=\text{N}$ at a relatively low temperature region. It was reported that $\text{C}=\text{N}$ absorption is seen to increase and to be followed by broader absorption at lower frequencies due to conjugated carbon–nitrogen sequences, this broad absorption becoming relatively more intense as the conjugated se-

quences increase in length, which results in the coloration of PAN.^{14–17} Therefore, it is believed that the red shift of UV absorption maximum (Fig. 5) and the exothermic peak in DSC (Fig. 4) are the result of the conversion of the nitrile group to the tetrahydronaphthyridine ring¹⁸ in this ternary polymer hybrid system, comprised of PAN, zinc chloride, and water. When we consider the acidic nature of aqueous zinc halide solution as shown in Table I, it is postulated that the polymerization of the nitrile group in the polymer hybrid system to give conjugated sequences is accelerated by zinc chloride, as it has been reported by Grassie et al.¹⁴ that the polymerization of the nitrile group is accelerated by nucleophilic reagents such as acids and phenols. It is worth noting that the relative absorption intensity at 2270 cm^{-1} to that at 2240 cm^{-1} gradually increases with a rise in temperature. This is ascribed to the increase in the nitrile group in the complexed state due to the loss of water, a competitor for the ligand site.

Because the polymer hybrid systems contain zinc chloride and water, it was expected that the hybrid polymer is electrically conductive. The results of the electric conductivity measurement are summarized in Table III. It is very interesting that a hybrid PAN system having a relatively high electric conductivity can be obtained from the one-step photopolymerization process. The conductivity of the hybrid PAN system increases with the increasing mol fraction of zinc chloride; however, its dependence on the mol fraction of zinc chloride is not as significant.

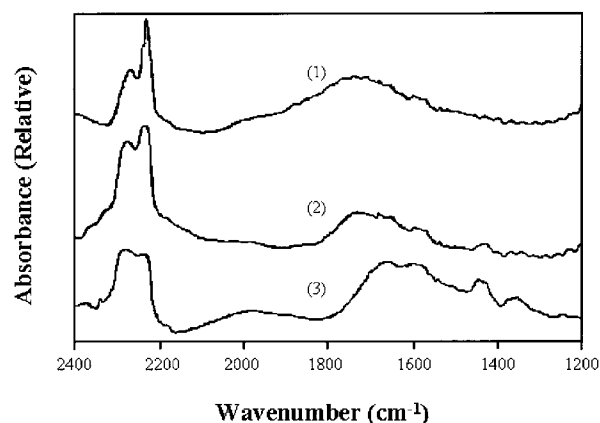


Figure 6 IR spectra of the hybrid polymer films, consisting of ZnCl_2 , PAN, and H_2O . Composition of the hybrid system are same as that given in Figure 5. (1) Before heat treatment, (2) after heating to 100°C , (3) after heating to 170°C .

Table III Electric Conductivity of the Hybrid Polymer Systems of Various Compositions

Compositions of Polymer Hybrid System, Expressed in Molar Ratio of			Conductivity 10^{-1} Scm^{-1}
ZnCl ₂ :	PAN (AN base) :	H ₂ O	
1	2	3	0.56
1	2	2	0.60
1	1	2	0.63

CONCLUSIONS

Although the initiation mechanism is not clearly understood, a transparent, rubbery polymer hybrid systems, consisting of PAN, zinc chloride, and water, has been prepared from one-step photoinduced polymerization of AN in a concentrated aqueous zinc chloride solution. It was explained that the photoinitiation and enhanced polymerization rate was ascribed to the σ -type complex of AN with the zinc ion.

However, any attempt to remove zinc chloride from the reaction mixture was not successful, due to the insolubility of the resultant polymer having a crosslinked structure to any conventional solvent due to the crosslinked structure.

It was found that the transparent colorless hybrid polymer systems, consisting of zinc chloride, PAN, and water, are electrically conductive, and the pendant nitrile group of PAN is easy to polymerize to form a tetrahydronaphthyridene ring

structure upon heating to 170°C by a complex formation with zinc chloride.

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