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Electrical Conductivities Of Poly (Alkyl Vinyl Ketones) Reacted With Dopant Solutions

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Poly ethyl vinyl ketone (PEVK) and poly methyl vinyl ketone (PMVK) were prepared using photochemical processes. The irradiation of monomers with UV light provides a new method, different from the methods previously used for the polymerization of these monomers. FTIR and UV spectroscopies were used for the structure and reaction mechanism of the polymers. NMR was used to calculate the conversion percentage of MVK and EVK polymers.

The conductivity change at various temperatures was traced during reactions of PMVK and PEVK with various dopant concentrations and the activation energy of these reactions were calculated by adding dopants and by adjusting the reaction conditions. A new method was developed to increase the conductivity of PMVK and PEVK polymers.

Introduction

The development of conducting polymers can be traced to the mid 1970 s when researchers at the University Pennsylvania reported that films of polyacetylene could be rendered conducting by doping reactors with a suitable electron withdrawing group or electron donating group.[1,2] Since that time, several other conducting polymers have been discovered.

Historically, only metals are regarded as conductor, while organic polymers are insulators (polyethylene, polystyrene). Some polymers poly(N-vinyl carbazole) conduct electricity under the influence of light and are used in the electrophotography industry.[3,4] Other polymers undergo pyrolysis to yield characteristics that exhibit moderate conductivity.[5]

A major discovery of the 1970 s was that certain polymers, notably poly sulfur nitride[6] and polyacetylene[7], can be made highly conducing in the presence of certain additives called dopants.[8] The mechanism of conduction is still not completely understood, but certain structural features are known to influence the level of conductivity. These include: delocalization (charge may be transferred through pendant groups); doping (by additional groups rearranging double bonds into a conjugated conducting mode)[9]; morphology (configurational and confomational factors. e.g.: conductivity of transpolyacetylene is greater than its cis form.)[10,11]

The dopant forms a charge-transfer complex with the polymer that is bellieved to give rise to highly delocalized cation radicals or anion radicals, depending on whether the dopant is an electron acceptor or donor, respectively. The delocalized regions are called solitons, which may be neutral (radical), positive (carbocation), or negative (carbanion). Conduction is believed to involve the intramolecular and intermolecular movement of electrons via the positive or negative solitons.

Conductors have a half-filled bond. It resembles a half-filled garage which offers maximum capacity for moving cars in and out. Here the conductivity decreases with increasing temperature. This can be explained by a Fermi-Dirac equation:[12]

$$P = \frac{1}{e^{(E-Ef)/k}+1} \tag{1}$$

where P is the population of the orbital, and E_f is the Fermi energy, the energy of the level for which P = 0.5 (half filled). For energies well above the Fermi energy, level 1 in the denominator can be neglected. Then Equation 1 can be converted into an equation which resembles a Boltzman distribution, where the population (P) decays exponentially with increasing temperature (Equation 2).

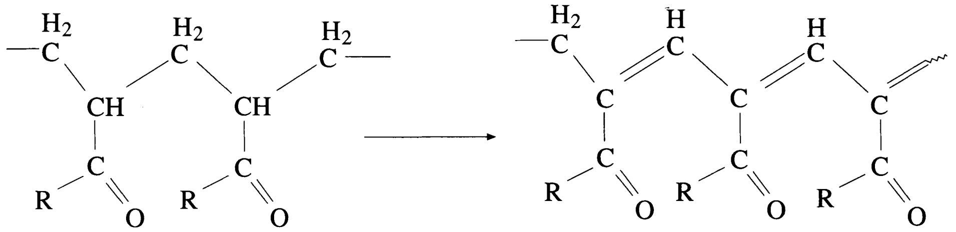
$$P = e^{-(E-E_f)/kT} \tag{2}$$

As a result the electrical conductivity of a conductor decreases with increasing temperature even though more electrons are excited into empty orbitals. In the semiconductors the energy gap between the filled valence and the conduction band is small, thermal excitation produces few electrons in the upper band and few holes in the lower band, and conductivity increases with increasing temperature. Another method for increasing the conductivity of semiconductors is increasing the number of charge carriers of a solid by implanting foreign atoms. If dopants can withdraw electrons from the filled valence bond, holes are created, which allow the remaining electrons to move freely (p-type semiconductor), where the holes are relatively positive to the electrons in the bond. Alternatively, if a dopant carries excess electrons, the additional electrons occupy empty bonds, giving n-type semiconductivity where n denotes the negative charge of the carriers.[12]

Polymerization of EVK and MVK:

Ethyl vinyl ketone (EVK) and methyl vinyl ketone (MVK) are polymerized in bulk using an azo initiator, 2,2'-Azobisisobutyronitrile (AIBN). It is unlikely that carbon-to-carbon double bonds are introduced into the polymer chains during polymerization.

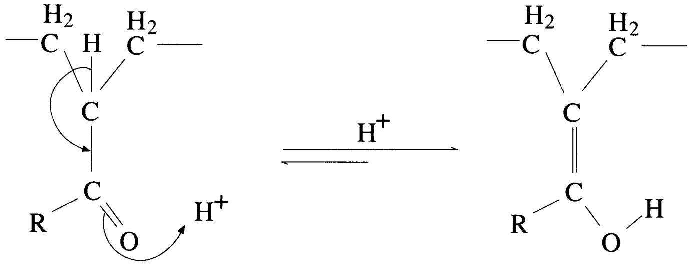
Previously, the reaction of poly alkyl vinyl ketones with active chloride, such as phosphoryl chloride ($0 = PCI_3$), to obtain the corresponding poly (acyl acetylenes) and the changes in the conductivities of phosphoryl chloride have been described.[13,14,15] Equation 3 indicates the general structure when poly vinyl ketones (PVK) react with active chlorides, [15] and summarizes the reaction mechanisms given in Equations (4-6):



(3)

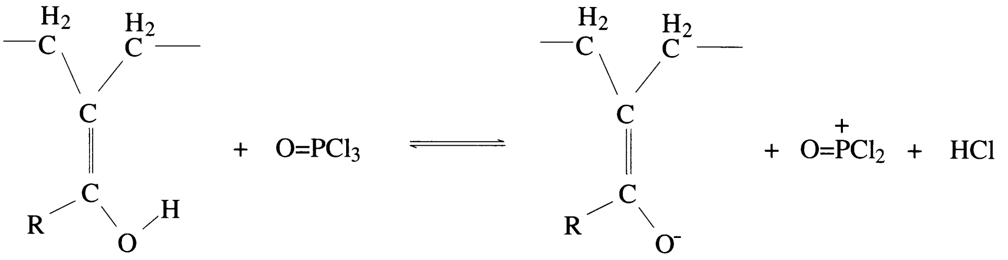
where R = $-CH_3$ or $-CH_2CH_3$.

Poly vinyl ketones with a tertary α-hydrogen have higher enol contents than the ketones with primary and secondary hydrogens. A trace amount of hydrochloric acid, contained in phosphoryl chloride as an impurity will promote the keto-enol tautomerism[13] as given in Equation (4):



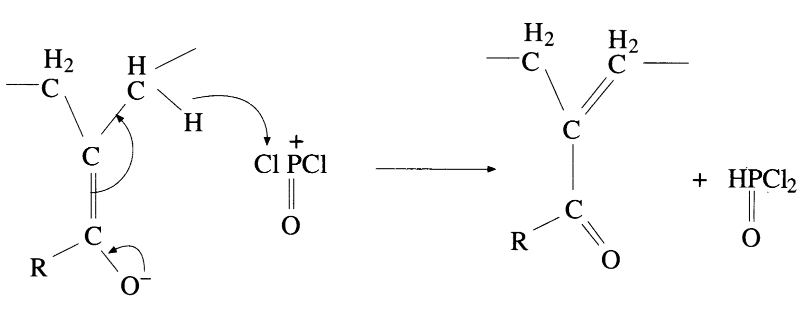
(4)

It is possible that the hydroxyl groups react with the active chloride as given in Equation (5):



(5)

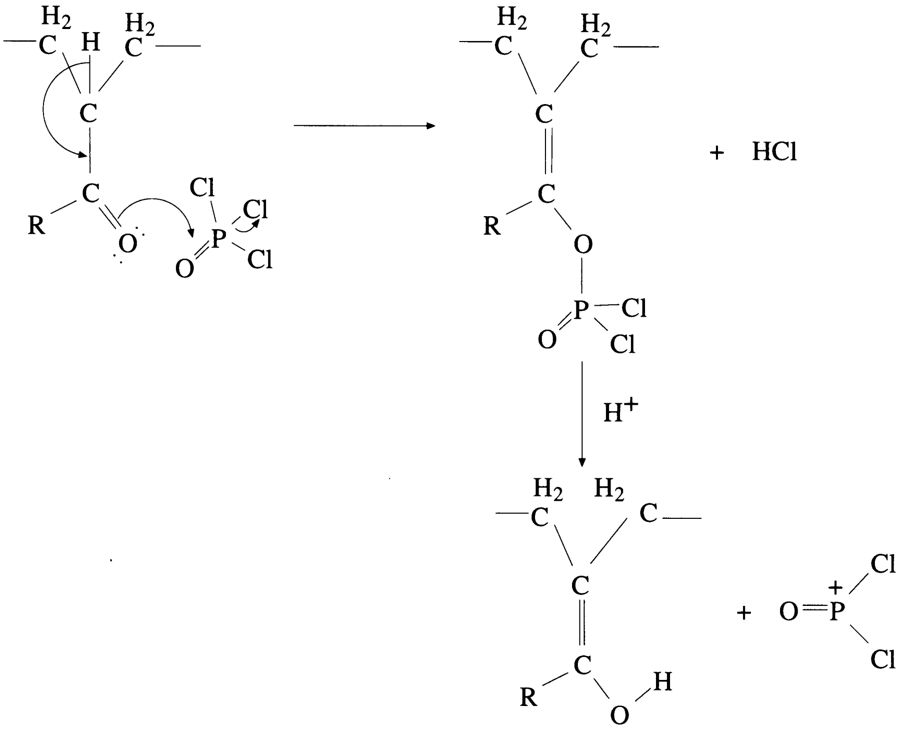
Although the above reactions seem to be reasonable, it is difficult to predict the subsequent steps. The following speculation is made tentatively, as given in Equation (6), which will consequently give the chain shown in Equation (3).



(6)

The way C - C double bonds are introduced into th polymer chains is shown in Equation (3).

Even though one assumes that there is no trace amount of HCI present in the phosphoryl chloride, eventually, by hydrogen-atom abstraction of phosphoryl chloride from the monomer molecule, the medium becomes acidic as shown in Equation (7) and the same reactions given in Equations (5) and (6) will be repeated:



(7)

In this study, poly methyl vinyl ketone (PMVK) and poly ethyl vinyl ketone (PEVK) were directly used in chloroform solution in the presence of phosphoryl chloride. The reaction mechanism in Equation (4) is very likely because of the higher enol contents of ketones where they contain tertiary α-hydrogen and their ability to transform this into carboxyl-group oxygen. Equations (5) and (6) show the completion of the reactions. A double bond is transferred to the main chain and conjugation, which is responsible for the increase in conductivity, is maintained.

Experimental and Discussion

Materials and Instruments:

Ethyl vinyl ketone (EVK) and methyl vinyl ketone (MVK) monomers, products of the Aldrich Chemical Company, were purified by distillation at 85° C and 82-85° C, respectively, at atmospheric pressure.

The 2-2'-Azobis isobutyronitrile (AIBN) initiator was a product of Polyscience Inc, and was purified by recrystallization from methanol twice before use as follows: a solution was prepared in methanol and cooled. The crystals were collected on a fritted glass filter and dried in a vacuum at room temperature.

The phosphoryl chloride ($0{=}PCI_3$) used was also a product of the Aldrich Chemical Company. Since it is highly corrosive and toxic, it was kept in a nitrogen atmosphere until use.

For UV irradiation, a Philips HPR, 125W mercury vapor lamp with a maximum wavelength of 254 nm was used.

UV spectra were performed with a Perkin-Elmer Lambda 3B UV/visible spectrophotometer, equipped with a P-E 3600 data station and a P-E 660 printer. NMR spectra were performed Varian 360L 60 MHz NMR. FTIR skpectra were performed with a Midac Corporation M 1200 spectrophotometer equipped with a Digital DEC computer, 316 SX Monitor, and HP Laser Jet 4 printer.

Film thicknesses were determined using a Dial Indicator from the Esterline Federal Corporation (Cat.

No. 22P-10). A Sargent Welch power supply, a Cenco milliampere meter and a Precision voltmeter (283 digital Multimeter) were used for determining the conductivities of the polymer films, applying the "four-probe technique".

Conductivity in solution was measured using an Oyster conductivity/temperature kit (Catalog No. 341655) from Extech Instruments. This has a glass conductivity cell and measures conductivity from 0.1 to 200,000 μS/cm, accurate to 0.5 % in four ranges, and takes temperature measurements from -30 to 105° C with $\mp$0.2° C.

For irradiation, quartz tubes of 12 cm height and 2.8 cm diameter were used.

A high vacuum system was used for evacuating and degrassing the monomer solutions to maintain a pressure of 10^{-4}-10^{-5} nm Hg.

Preparation of Polymers:

About 5 mL distilled MVK, 5 mL benzene and 1.0 % initiator (AIBN) were introduced into a quartz tube, and the tube was sealed with a septum. The system was evacuated to a pressure of 10^{-5} mm Hg in 5-6 hours. The tube was then put under UV light in a horizontal position, about 20 cm below the source. After irradiation for the period required for polymerization (usually 3 hours), the obtained polymer was dissolved in chloroform, which is a good solvent for both monomer and polymer, and precipitated in methanol. The obained polymer was filtered and dried in a vacuum oven at 25-35° C. Poly (ethyl vinyl ketone) was prepared using the same procedures as the poly (methyl vinyl ketone) polymerization. However, another method can also be used for polymerization. The distilled monomer is polymerized in bulk at 50° C in benzene (50% v/v) using an azo catalyst (AIBN) as an initiator for the low-molecular-weight polymer, and at room temperature without any initiator for the high-molecular-weight polymer.[15] According to the method of McMahon, EVK is polymerized at 50° C in bulk using the same initiator mentioned above.[15,16]

Poly methyl vinyl ketone (PMVK) and poly ethyl vinyl ketone (PEVK) films were prepared by the casting of a chloroform solution of their polymers on a glass surface.

Conductivity Measurement of MVK and EVK Polymers in Solutions:

Methyl vinyl ketone (MVK) and ethyl vinyl ketone (EVK) monomers were polymerized by UV irradiation as explained above in "Preparation of Polymers." After irradiation, the obtained polymers were dissolved in chloroform and precipitated in methanol, and then filtered and dried in a vacuum oven at room temperature. The effect of phosphoryl chloride ($0{=}PCI_3$) dopant on those polymers in bulk solutions, was examined and the conductivity was measured directly, using a probe immersed in the solution.

About 0.125 g of solid polymer was dissolved in 12.5 mL chloroform and 0.625 mL phosphoryl chloride was added as a dopant.

Experimental Results and Discussion:

Figures 1 and 2 show the UV spectra of the PMVK and PEVK films. PMVK and PEVK show maximum absorption in the same region (282-288 nm respectively). Therefore, UV-spectroscopy would not provide good detection spectra for these two polymers. After dissolving the polymer in chloroform and adding phosphoryl chloride ($0{=}PCI_3$) as the dopant, the reaction was started at - 13° C (Figure 3). During the course of the reaction, the conductivity increased very sharply and at 0° C the reaction was completed. After the completion of the reaction, when the system was rapidly heated to rooom temperature the conductivity did not change.

Figure 4 shows the conductivity change of the system containing 0.125 g PMVK, 12.5 mL chloroform and 1.25 mL phosphoryl chloride at 0° C. After the reaction was completed at 0° C, the conductivity reched a constant value However, when it was heated slowly to room temperature, the conductivity increased sharply, as shown in Figure 5.

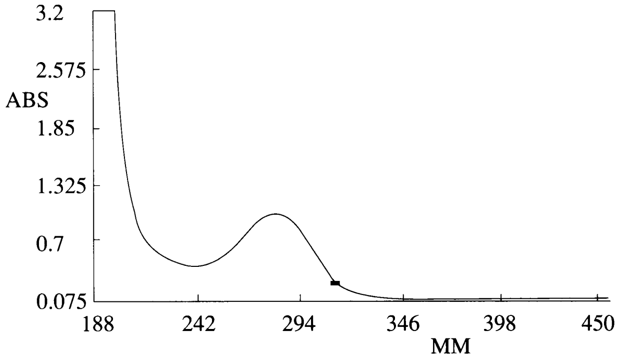


Figure 1. UV-absorption spectrum of PEVK

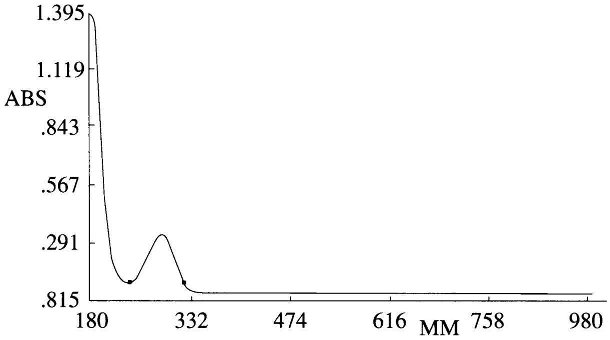


Figure 2. UV-absorption spectrum of PMVK

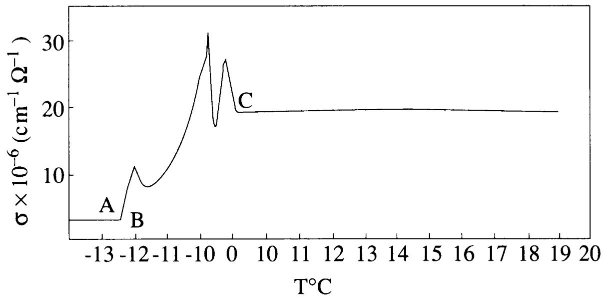


Figure 3. Temperature effect on the conductivity of PMVK reacted with $O=PCl_3$ (0.125 g PMVK + 12.5 mL $CHCl_3$ + 0.625 mL $O = PCl_3$)

A: Before adding dopant;

B: After adding dopant;

C: Reaction completed at 0° C

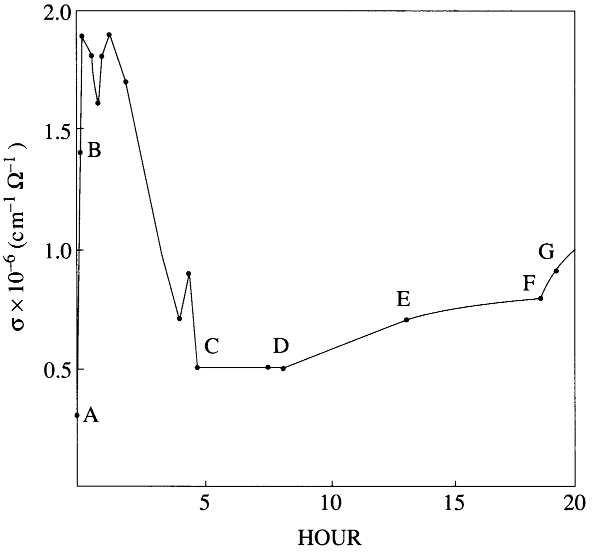


Figure 4. Reaction of PMVK with $O = PCl_3$ (0.125g PMVK + 12.5mL $CHCl_3$ + 1.25mL $O = PCl_3$)

A: Before adding $O=PCl_3$; B: After adding $O=PCl_3$;
C: Reaction completed at 0° C; D: Reation started to heat;
E: System at 0.2° C; F: system at 0.4° C;
G: System at 1.3° C

Figure 6 shows the conductivity change of PEVK after adding (0=PC1$_3$) in chloroform solution at 0° C. The reaction was completed within five hours at 0° C. Both PEVK and PMVK showed a sharp increase in conductivity during the reaction with phosphoryl chloride. After the completion of the reaction, conductivity became constant at 0° C.When the reaction was started at 0° C, the initial conductivity was $1.6\times10^{-6}\Omega^{-1}\mathrm{cm}^{-1}$. When the system was heated gradually to room temperature, conductivity reached a value of $8.0 \times 10^{-6} \Omega^{-1} cm^{-1}$ (Figure 7). Reactions of PEVK and PMVK with phosphoryl choride are highly exothermic, therefore reactions are completed at 0° C. In both cases after reaction is completed at 0° C, conductivity values become constant and heating to room temperature causes a sharp increase in conductivity if the heating is done slowly.

Figure 8 shows the conductivity charge of PEVK after adding $0 = PCI_3$ in chloroform solution at 25° C. When the reaction was performed at 25° C, before adding $0 = PCI_3$, σ_0=1.9-2.0 $\times 10^{-6} \Omega^{-1} cm^{-1}$. After $0{=}PCI_3$ was added at 25° C, it agin exhibited the same conductivity. After the system had been maintained at 25° C, for 26 hours the conductivity reached a value of $237 \times 10^{-6} \Omega^{-1} cm^{-1}$. The conductivit increased about 100 times and became constant.

In both cases (reactions at 0° C and 25° C) the same initial conductivity values were observed. After completion of the reaction, it was kept at 25° C, and conductivity increased continuously with time (Figure 8).

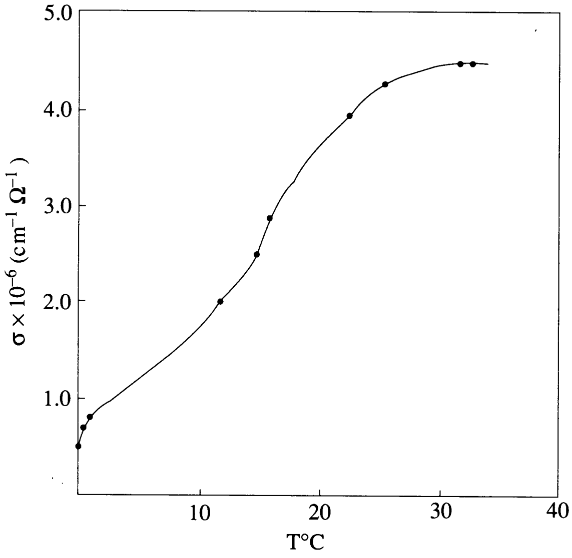


Figure 5. Temperature effect on the conductivity of PMVK after reaction with $O{=}PCl_3$ completed at 0° C (0.125g KMVK + 12.5mL $CHCl_3$ + 1.25mL $O{=}PCl_3$)

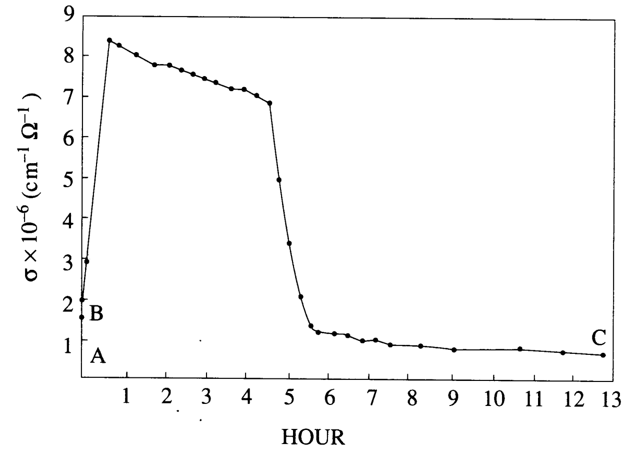


Figure 6. Conductivity change of PEVK during reaction with $O{=}PCl_3$ at 0° C (0.125g PEVK + 12.5mL $CHCl_3$ + 1.25mL $O{=}PCl_3$)

A: Before adding $O{=}PCl_3$; B: After adding $O{=}PCl_3$;
C: System heated at 3.5°C; Between B and C: 0.1-0.7°C

Acid-catalyzed aldol-type condensation between the carbonyl and methyl group took place when the temperature was raised. Conductivity increased with increasing temperature because of the resulting increase in the passage of electric current.

Determining Activation Energy In Reaction of PEVK and PMVK with Phosphoryl Chloride:

The measurement of the conductivity change with time is an excellent method for observing the kinetics of the reaction since the sudden increase in the conductivity during the reaction slows down and reaches a constant value at the completion of the reaction.

Figure 6 shows the conductivity change of PEVK after reaction with $0{=}PCI_3$(0.1 is g PEVK +12.5 mL $0{=}PCI_3$) at 0° C. 7.5 hours after the addition of $0{=}PCI_3$, the reaction was completed and conductivity became constant. To determine the activation energy, another reaction temperature was needed. The same experiment was carried out with another set, this time at 14.7° C. Figure 9 shows the plot for this. The sudden increase in conductivity reached a constant value 5.7 hours after the start time. Even though the rate law for the chemical reaction is not knowwn it is possible to use the Arrhenius expression to calculate the effect of temperature on the reaction rate. Suppose that the time required to reach he completion of reaction at two different temperatures, T_1 and T_2, are denoted by ζ_1 and ζ_2, then:

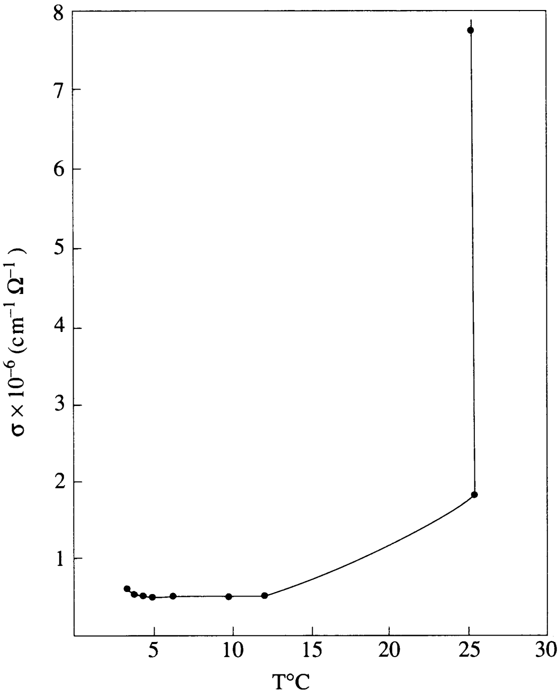


Figure 7. Temperature effect on the conductivity of PEVK after reaction with $O{=}PCl_3$ completed between 0.1-0.7° C

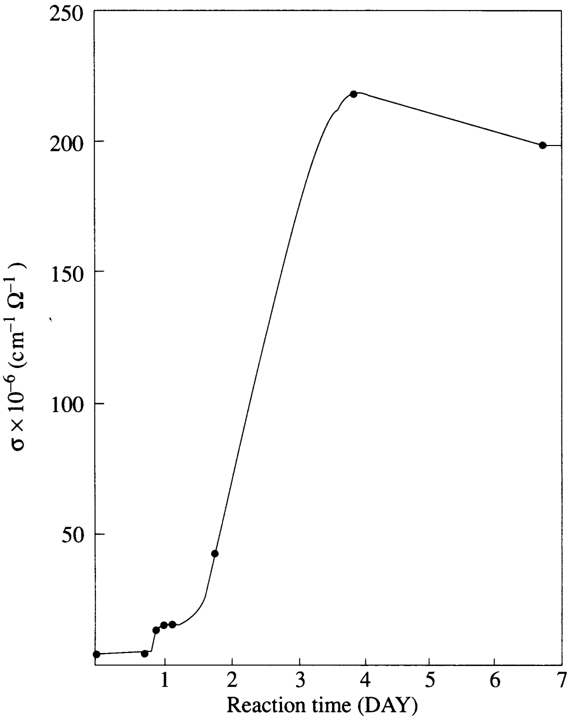


Figure 8. Conductivity change of PEVK after reaction with $O{=}PCl_3$ at 25° C (0.125g PEVK + 12.5mL $CHCl_3$ + 1.25mL $O{=}PCl_3$)

$$\frac{\zeta_1}{\zeta_2} = \frac{e^{-Ea/RT_2}}{e^{-Ea/RT_1}} \tag{8}$$

and

$$ln\zeta_1/\zeta_2 = Ea/R(1/T_1 - 1/T_2) \tag{9}$$

are obtained. From Equation (9), the activation energies E_a of the reaction of PEVK and PMVK with $0{=}PCI_3$ were determined.

The activation energy of he chemical reaction of PEVKwith phosphoryl chloride, calculated by taking ζ_1 to be 7.5 hours at 0° C and ζ_2 as 5.7 hours at 14.7° C, was found to be 12.18 kJ/mol (2.9 kcal/mol). Measuring the conductivity change throughot the reaction provides a convenient means of calculating the activation energy of the reaction of these polymers with doping solutions.

Figure 4 and Figure 10 show the plots for the conductivity change of PMVK in the presence of $0{=}PCI_3$ at 0° C and 14.9° C, respectively. The activation energy of this reaction is calculated by taking ζ_1 to be 5.0 hours at 0° C and ζ_2 as 2.8 hours at 14.9° C (Figure 10). It was found to be 25.3 kJ/mol (6.1 kcal/mol). Since reactions with PMVK are faster, the activation energy of this reaction is higher than the one obtained with PEVK, considering that both reactions are exothermic and, as temperature increases, the reaction rate slows down.

NMR Study of MVK and EVK Polymers:

The conversion percentages of PMVK and PEVK were determined using NMR spectroscopy. Five mL monomer, 5 mL benzene and 1.0 % (AIBN) initiator were put into a quartz tube. The tube was connected to a vacuum line and degassed to 10^{-5} mm Hg and irradiated with UV rays for different time periods. After a certain irradiation period, a sample was removed with a syringe from the irradiation tube, and the NMR spectrum was performed immediately. For high conversion, polymer solutions were diluted with deuterochloroform. Conversion percentages were calculated from the height of each integral line, both for the monomeric and irradiated samples (Figure 11-14). The peaks at (A) in these figures are attributed to the $=CH_2$ functional group in the monomer. Since polymer conversion is directly proportional to the $=CH_2$ bond opening, the decrease in integral peak height is proportional to the degree of polymerization.

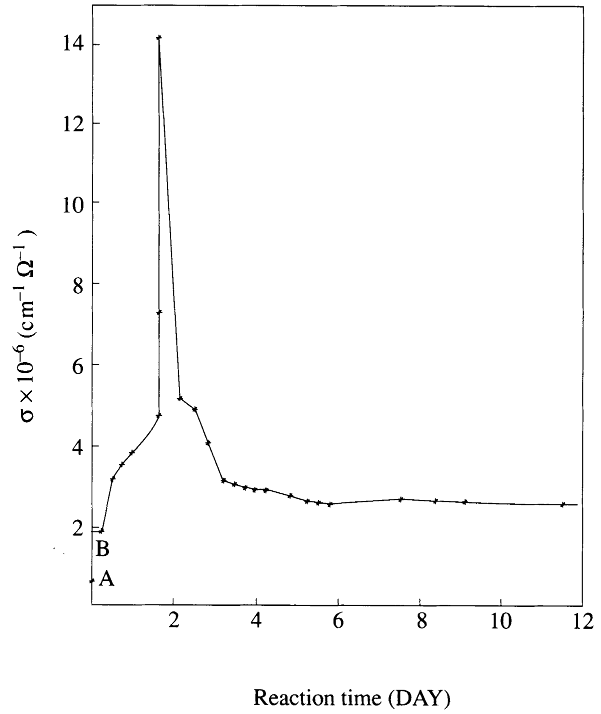


Figure 9. Conductivity change of PEVK during reaction with $O{=}PCl_3$ at 14.7° C (0.125g PMVK + 12.5mL $CHCl_3$ + 1.25mL $O{=}PCl_3$)

A: Before adding $O{=}PCl_3$;

B: After adding $O{=}PCl_3$

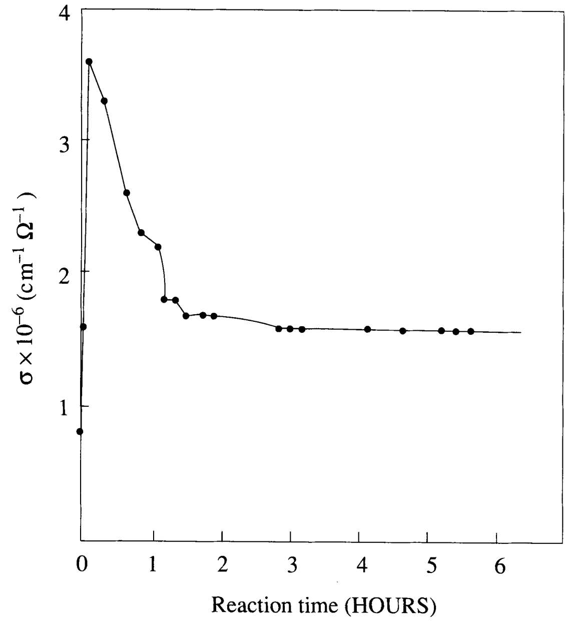


Figure 10. Conductivity change of PMVK during reaction with $O{=}PCl_3$ at 14.9° C(0.125g PMVK + 12.5mL $CHCl_3$ + 1.25mL $O{=}PCl_3$)

The conversion percentage is calculated from the height of each integral line for the irradiated samples by comparing the height for the monomic MVK and EVK at zero time irradiation as follows:

$$Conversionpercentage = (H_0 - H_i) \times 100/H_0 \tag{10}$$

where H_0 = height of integral line at zero time irradiation, and H_i= height of integral lin at irradiation time t.

Figures 11 and 12 show NMR specra of MVK monomer and PMVK after 5 hours of irradiation. Figures 13 and 14 show the NMR spectra of EVK monomer and its polymer after 3 hours of irradiation. Figures 15 and 16 show the plots for conversion percentage versus irradiation time of the free-radical polymerization of MVK and EVK initiated by UV irradiation at 25 ° C. The free-radical polymerization is explained by the kinetic equation:[17,18]

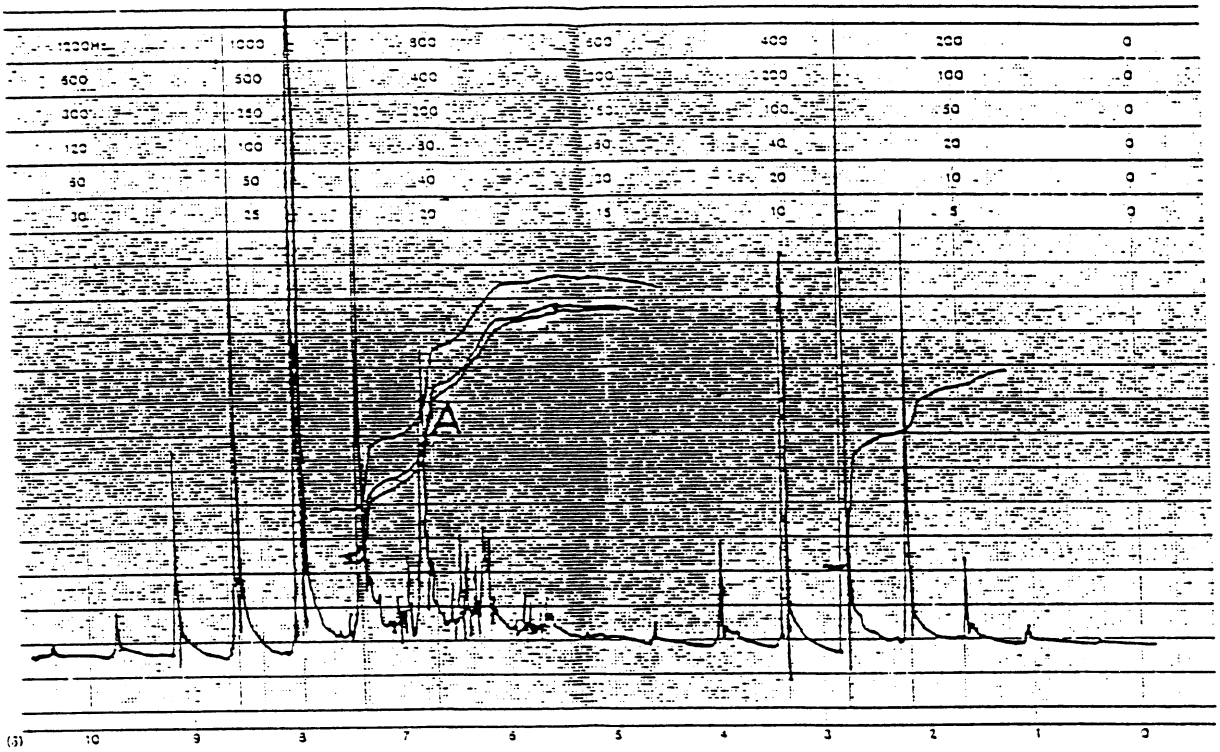


Figure 11. NMR spectrum of MVK monomer

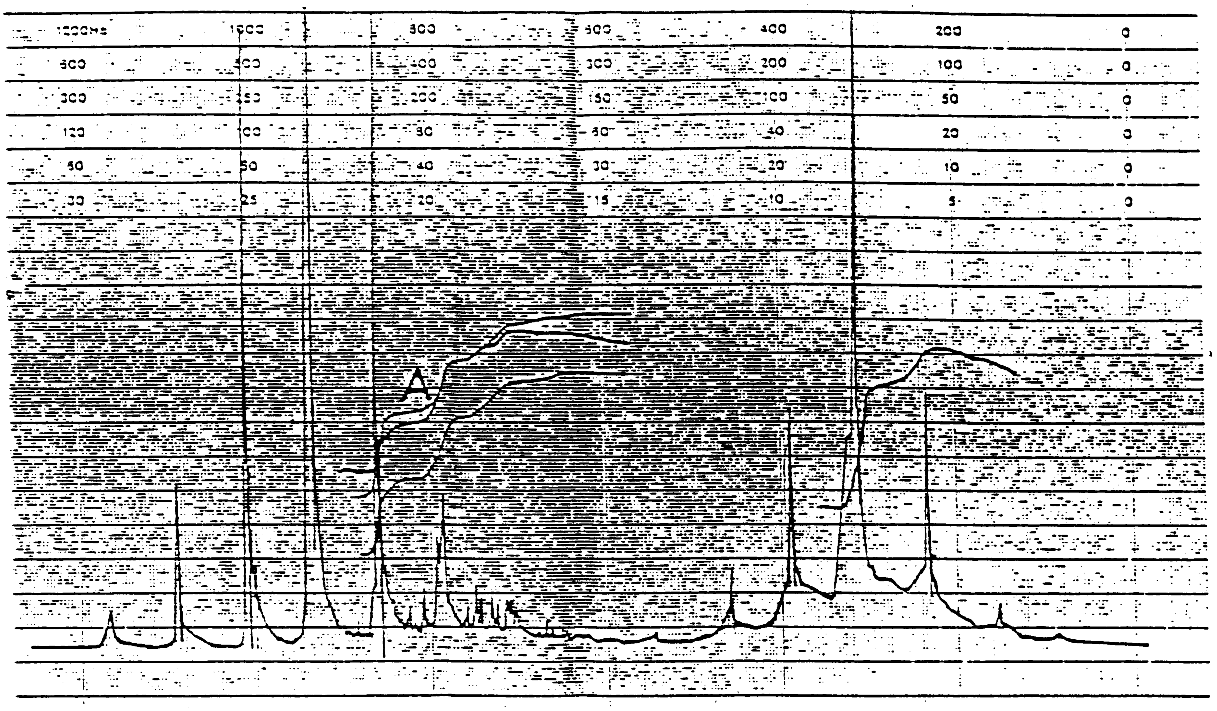


Figure 12. NMR spectrum of PMVK after 5 hours of UV irradiation

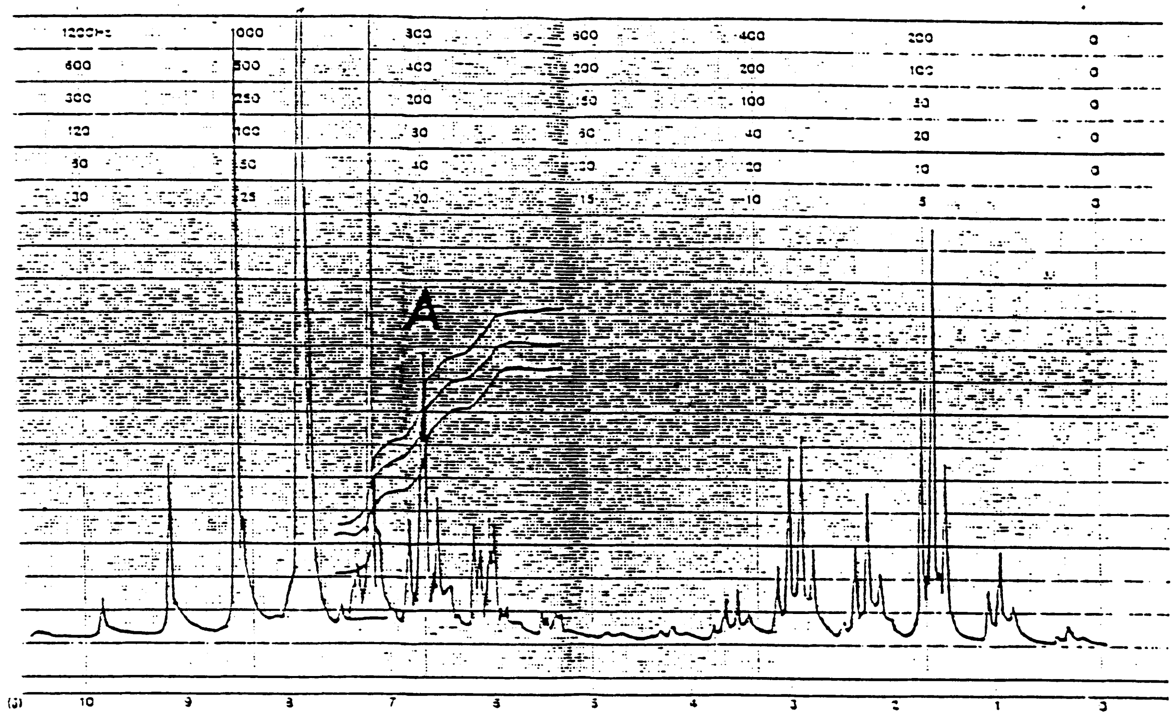


Figure 13. NMR spectrum of EVK monomer

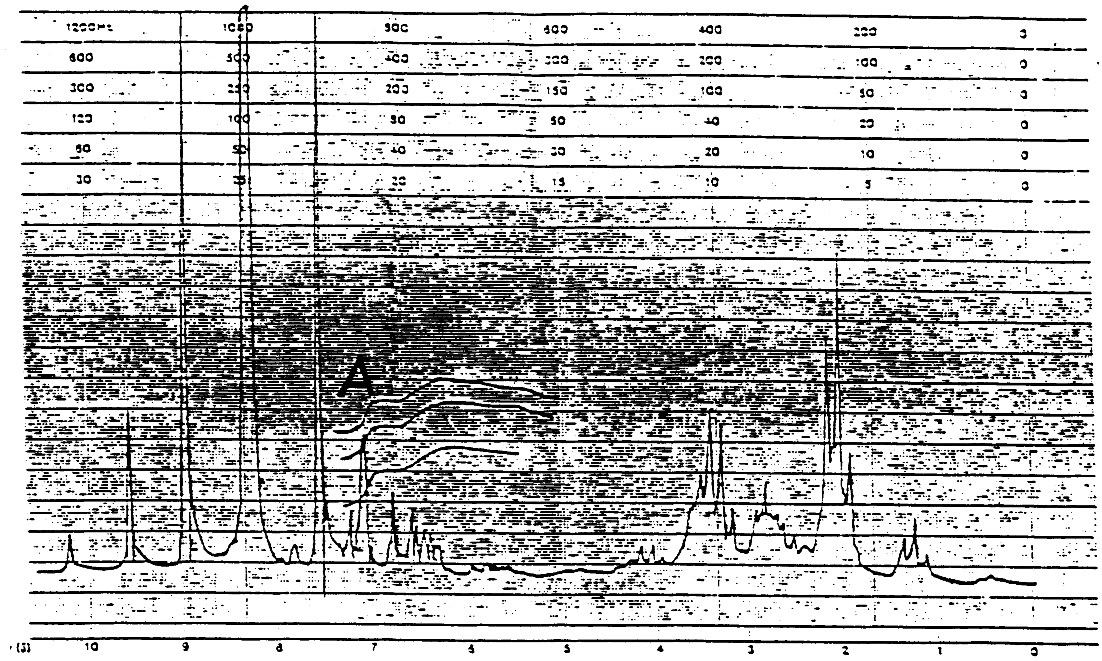


Figure 14. NMR spectrum of PEVK after 3 hours of UV irradiation

$$- d[M]/dt = k_p(fk_i/k_i)^{1/2}[I]^{1/2}[M] \tag{11}$$

where f is the efficiency factor (fraction of the initiator starting polymerization) and k_i, k_p and k_t are the rate of initiation, propagation and termination, respectively. (I) is one initiator concentration and [M] is the monomer concentration. The integrated form of the above equation is:

$$ln[M_0]/[M] = k_p(fk_i/k_i)^{1/2}t \tag{12}$$

Therefore, a plot of $\ln[M_0]/[M]$ versus irradiation time should give a straight line. Figure 17 indicates such a plot both for PMVK and PEVK. Here $\ln[M_0]/[M]$ is approximately equal to $\ln(H_0/H_t)$ and calculated taking $[M_0]$ as the non-irradiated monomer concentration and [M] as the concentration at irradiation time t. Both H_0 and H_t are measured from the height of the integral line obtained for the peaks (A) in Figures (11-14). Two different slopes, obtained for both polymers, correspond to two different rate constants (Figure 17). The sudden acceleration on the PMVK curve can be explained by the Norrish-Smith (autoacceleration) effect.

Conclusion

The main aims of this study were: first, to prepare some conductive polymers by applying new and effective methods to obtain high conversions; then, to obtain maximum conductivity by varying the reactant concentrations or by adding dopant solutions.

In this study, PEVK and PMVK were prepared through photochemical processes. The irradiation of monomers with UV light is a new method, different from the methods previously used for the polymerization of these monomers.[15] The monnomer solutions with initiator were irradiated with UV rays and polymerization proceeded via a free-radical mechanism. This proved to be an efficient method, which led to high conversions. PMVK reached about 80 percent conversion after seven hours of irradiation (Figure 15). EVK polymerization initiated by UV light reached about 60 percent conversion after four hours of irradiation (Figure 16).

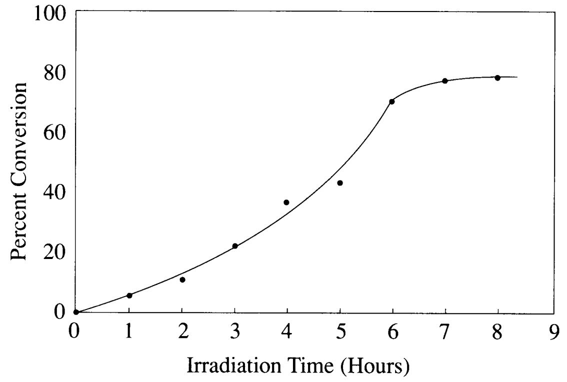


Figure 15. Free-radical polymerization of MVK initiated with UV irradiation at 25 °C

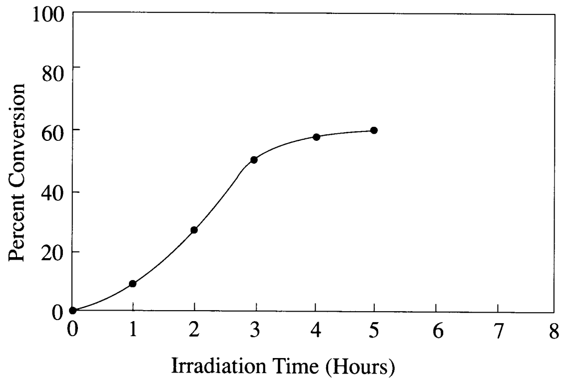


Figure 16. Free-radical polymerization of EVK initiated with UV irradiation at 25 °C

If the thermal and electrical stability of conductive polymers at elevated temperatures could be determined in kinetic studies, it would be very useful for improving the properties of conductive polymers.

With both PMVK and PEVK, conductivity increases with temperature (Figures 5 and 7). However, it is known that in conductors conductivity shows an inverse relationship to temperature. In a semiconductor, conductivity increases with increasing temperature. Since the conductivity of PMVK and PEVK increases with temperature, they behave like semiconductors. The conductivity of a semiconductor can be measured using two methods: 1) increasing the temperature; 2) increasing the number of charge carriers of a solid by implanting foreign atoms (dopants).[19] The increase in conductivity values by introducing dopants into these polymers confirms the above agreement.

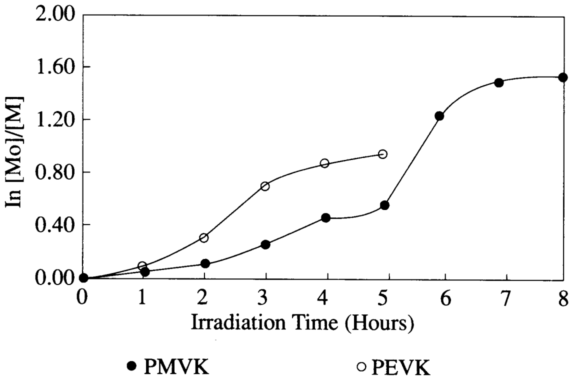


Figure 17. Rate of formation of polymers as a function of irradiation time

The measurement of the conductivity change with time after the addition of a dopant is an excellent method of following the kinetics of a reaction. The sudden increase in conductivity during a reaction slows down and reaches a constant value at the completion of the reaction (Figures 3, 4, 6, 9, 10). By tracing the conductivity charge in bulk solutions of polymer when they are reacted with dopants, the exact time of starting and ending a reaction can easily be determined. This helps to determine the kinetics of the reaction mechanism and the activation energy of the reaction. In both cases, the conductivity of the MVK and EVK polymers showed a sharp increase during the course of the reaction with the dopant ($0= P Cl_3$). After the completion of the reaction, conductivity became constant, returning to its initial value. If the system was heated rapidly, it did not change. However, if system was heated slowly, its conductivity increased to almost 10 times the initial value.

In future work, the effect of some other dopants on the conductivity of other conductive polymers, such as AsF_5 for poly acetylene, Br_2 for poly sulfur-nitride, BF_4^- ion for poly ethylene oxide polymers. The most effective concentrations of these dopants will be determined using the same methods developed in this study.

The degradation kinetics of these conductive polymers will be investigated and the most stable conditions with the poroper dopant for these polymers will be evaluated following the same procedure applied here.

In this study, a new method was developed to increase the conductivity of polymers by adding dopants and by adjusting the reaction conditions.

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