

Photocatalytic Degradation of Poly(ethylene oxide) and Polyacrylamide

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ABSTRACT: The photocatalytic degradation of poly(ethylene oxide) (PEO) and polyacrylamide (PAM) was investigated using combustion synthesized nano-sized TiO₂ catalyst (CSN-TiO₂). The degradation was conducted with two different UV lamps of 125 and 80 W. Degradation of PEO was observed in both the cases, whereas PAM degraded only when exposed to lamp of higher power, even in the presence of catalyst. Gel permeation chromatography was used to determine the molecular weight distribution. Continuous distribution kinetics was applied to determine the kinetics of the photodegradation process. The degradation rate coefficients of the polymers in the presence of combus-

tion synthesized TiO₂ were higher than the degradation rate coefficients obtained with commercially available TiO₂ (Degussa P-25). The enhanced degradation rate of the polymers when catalyzed by CSN-TiO₂ can be due to the nano-size, high surface area, and the presence of hydroxyl groups on the surface of the catalyst. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3997–4003, 2006

Key words: photocatalytic; degradation; TiO₂; Degussa P-25; combustion synthesized catalyst; lamp power; rate coefficients

INTRODUCTION

Water-soluble polymers form a major class of polymers that are versatile and have wide spread applications. Among these polymers, polyacrylamide (PAM) and poly(ethylene oxide) (PEO) are important polymers that have enormous practical utility in various branches of industry. PAM is mainly used as flocculant in water treatment, in enhanced oil recovery, in biomedical applications,^{1,2} and as thickening agent in paper and textile industry.³ Similarly, PEO has also several applications as surfactant, as vehicles in drug release, and in colloidal stabilization.^{4–6} Hence, it becomes imperative to understand the degradation of these polymers by different routes, especially when they become potential contributors to environmental problems and when they are discarded from industries.

The photodegradation of polymers is mainly photooxidative due to the presence of oxygen, which results in reduction in molecular weight, introduction of new functional groups, and also the possibility of crosslinking.⁷ PEO is a simple linear chain polymer

that has only carbon–carbon, carbon–hydrogen, and carbon–oxygen bonds. PAM has only carbon–carbon and carbon–hydrogen bonds in its backbone with the amide group as pendant group. The photodegradation is triggered by the formation of macroradical due to hydrogen abstraction from the main chain.⁸ The photostability of PEO and its complexes with various metal salts has been extensively studied. The ability of PEO to bind to different cations reduces the photostability of PEO.^{9–12} Chain scission of PEO occurs resulting in the formation of esters, aldehydes, and formates. The differences between photooxidation and thermooxidation lies in the amount of esters and formates formed. Thermooxidation produces equal amounts of both esters and formates, whereas photooxidation generates formates to esters in a ratio of 5:1.¹³ PAM is also susceptible to photodegradation, but there are arguments about its tendency to degrade to monomer.^{14–17} The carbon-centered radicals of PAM have been reported to be very sensitive to the presence of oxygen and can lead to a variety of photooxidative reactions.¹⁸ TiO₂ and metal-substituted TiO₂ are well known semiconductor photocatalysts used for photodegradation of dyes,^{19–24} surfactants,^{23,25} toxic organic compounds like phenols,^{26–28} oxalates,²⁹ pesticide pollutants,³⁰ and in the degradation of polycarbonate.³¹

In this study, the kinetics of photodegradation of PEO and PAM was investigated with combustion synthesized nano-sized TiO₂ catalyst (CSN-TiO₂), and the

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degradation rates were compared with the rates obtained with commercial TiO_2 (Degussa P-25) and without any catalyst. The effect of varying the intensity of UV radiation on the photodegradation of the polymers was also investigated. Continuous distribution kinetics was applied to model the kinetics of the process and to determine the degradation rate coefficients.

EXPERIMENTAL

Materials

PAM was synthesized from the monomer by reacting with 0.03 g/L potassium persulfate and isopropanol in aqueous solution at 60°C . Nitrogen was continuously flushed in to the solution. The polymer was precipitated with methanol and dried in an oven at 60°C until constant weight was obtained. PEO was obtained from Aldrich chemicals. The number average molecular weight was determined using gel permeation chromatography (GPC) and was 1.97×10^5 g/mol and 1.64×10^5 g/mol for PEO and PAM, respectively.

Synthesis and characterization of catalyst

The solution combustion method was used for the preparation of anatase CSN- TiO_2 . It was prepared by using titanyl nitrate as precursor with oxalyldihydrazide as fuel. The details of preparation are given elsewhere.²⁴ The catalyst was characterized using X-ray diffraction, BET surface area, TGA/DTA, UV, and IR spectrometer. The catalyst is nano-sized, crystalline and has a higher surface area ($156 \text{ m}^2/\text{g}$) than the commercial Degussa P-25 ($11 \text{ m}^2/\text{g}$). The catalyst has more surface hydroxyl groups, as evidenced by TGA/DTA.²⁴ The catalyst also has a reduced band gap²⁴ of 2.18 eV, as shown in the optical absorbance spectra (Fig. 1). Commercial Degussa P-25 TiO_2 shows a single peak at 400 nm (which corresponds to a band-gap energy of 3.10 eV), while the combustion synthesized TiO_2 shows two optical absorption thresholds at 570 and 467 nm that correspond to the band gap energy of 2.18 and 2.65 eV, respectively. The decrease in the band gap of the combustion synthesized catalyst was attributed to the carbide ion substitution for oxide ion in the TiO_2 , and thus the optical absorption spectra of combustion synthesized catalyst was similar to that of carbon substituted TiO_2 .²⁴ These properties make it an attractive and potential catalyst for use in photodegradative studies.

Photochemical reactor

A high-pressure mercury vapor lamp of 125 and 80 W (Samson lamps, Philips lamps) was used as light

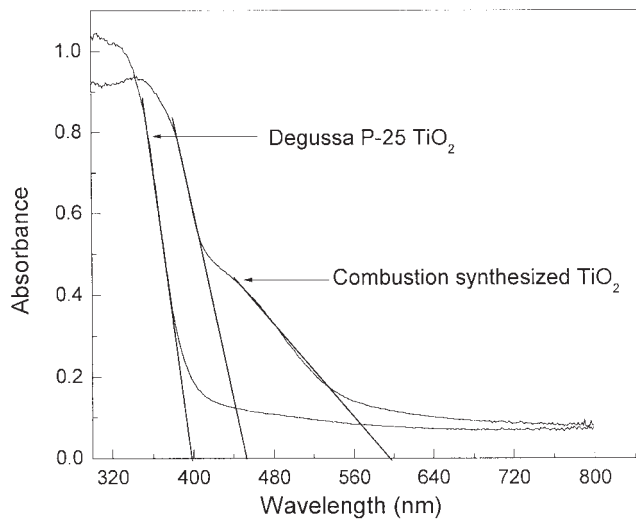


Figure 1 Optical absorbance spectra of Degussa P-25 and CSN- TiO_2 .

source by removing the outer cover. It was placed in a jacketed quartz tube (for cooling by water circulation) of 3.4 cm inner diameter, 4 cm outer diameter, and 21 cm length. The reaction vessel was a glass cylinder of 6 cm inner diameter and 16 cm height. The polymer sample solution was stirred with a magnetic stirrer and was placed 3 cm above the stirrer. The lamps emitted predominantly at 365 nm and the photon flux was 5.4×10^{-6} mol of photons/s and 3.5×10^{-6} mol of photons/s for 125 and 80 W lamps, respectively.

Degradation experiments

Aqueous solutions of polymer of concentration 2 g/L were used for all the experiments. Ninety milliliter of the solution was taken each time and the concentration of the catalyst was fixed at 2 g/L for all the experiments to study the kinetics of degradation. Samples of solutions were taken at various time intervals and the molecular weight distribution was obtained by injecting the samples in GPC. The samples were centrifuged and filtered to remove catalyst particles before analysis.

UV spectral analysis

The UV spectrum of the polymers before and after degradation was obtained by a spectrophotometer (Perkin-Elmer Lambda-35). The wavelength scanned was from 500 to 200 nm. No absorbance was observed beyond 500 nm.

GPC analysis

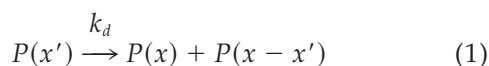
The samples were analyzed in GPC with double distilled deionized water as eluent at a flow rate of

0.5 mL/min. The column used was Waters Ultrahydrogel linear column measuring 7.8 mm × 300 mm maintained at 50°C. The refractive index was monitored continuously with a differential refractometer (Waters 401). A sample of 800 μL was injected into the system to obtain a chromatogram and converted to molecular weight by using PEO calibration standards.

RESULTS AND DISCUSSION

Theoretical model

Continuous distribution kinetics was applied to determine the kinetics of degradation of PEO and PAM. For a polymer of molecular weight, $P(x')$, the random degradation of the polymer chain is represented by



The population balance equation with k_d as the degradation coefficient is

$$\begin{aligned} \partial P(x,t)/\partial t = & -k_d(x) p(x,t) \\ & + 2 \int_x^\infty k_d(x') p(x',t) \Omega(x,x') dx' \quad (2) \end{aligned}$$

For random chain scission, the distribution of degraded products given by $\Omega(x,x')$ is $1/x'$.³² Assuming a linear dependence, $k_d(x) = k_d x$, the above equation reduces to

$$\partial p(x,t)/\partial t = -k_d x p(x,t) + 2 \int_x^\infty k_d x p(x',t) dx' \quad (3)$$

Applying moment operation to eq. (3) yields

$$dp^{(j)}/dt = -(j-1)/(j+1)k_d p^{(j+1)}(t) \quad (4)$$

For $j = 0$ and $j = 1$

$$\begin{aligned} dp^{(0)}/dt &= k_d p^{(1)}(t) \\ dp^{(1)}/dt &= 0 \end{aligned} \quad (5)$$

Solving the above equation with initial condition $p^{(0)}(t=0) = p_0^{(0)}$ and using eq. (4), the variation of number average molecular weight M_n , defined as $p^{(1)}/p^{(0)}$, with time is

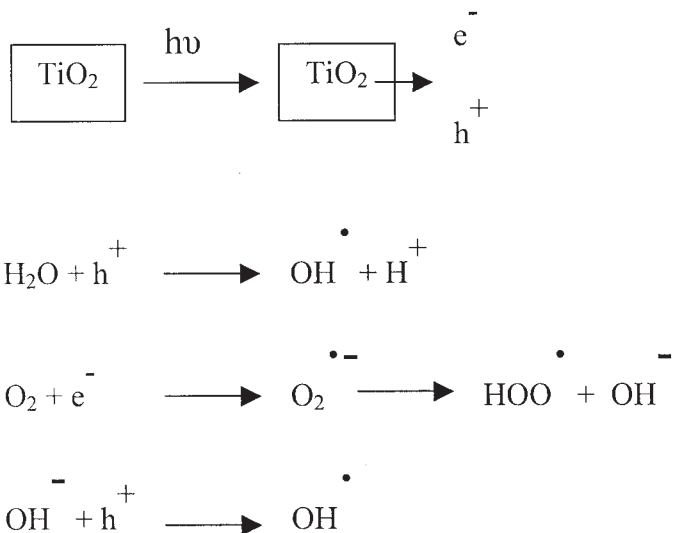
$$(M_{n0}/M_n) - 1 = k_d M_{n0} t = kt \quad (6)$$

Mechanism and kinetics of photodegradation

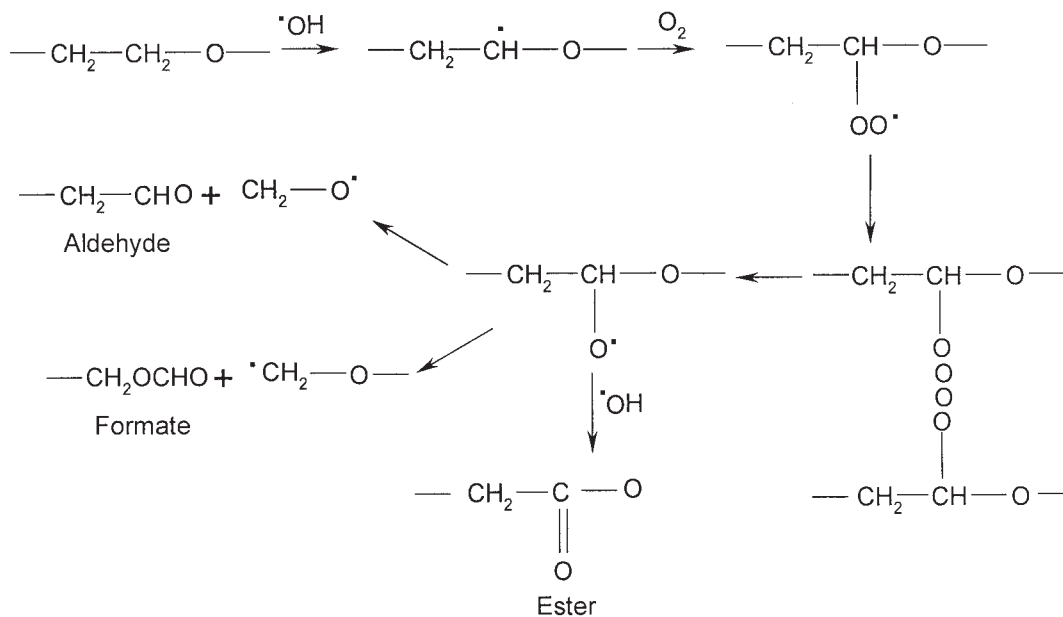
Photodegradation is mainly photooxidative wherein chain scission is triggered by hydrogen abstraction from main chain by a hydroxyl radical or reaction with oxygen to form peroxide radical. It was determined by Grollman et al.³³ that only 1% of the hydroxyl radicals formed are involved directly in main chain scission, whereas the remaining participate in hydrogen abstraction and other radical reactions for irradiation by high-energy rays. The enhanced degradation by CSN-TiO₂ is mainly due to the presence of large number of hydroxyl groups on its surface that help in the generation of many macroradicals. CSN-TiO₂ is supposedly known to possess nearly 10 times the number of hydroxyl groups on its surface than that in Degussa P-25.³¹ Because of its higher surface area and nano-size, it is a better catalyst than commercial Degussa P-25. Another important factor that contributes to it being an efficient catalyst for degradation is the reduced band gap. Therefore, an electron from valence band can move to conduction band easily creating a hole. This hole takes up an electron from surface bound hydroxyl species generating a hydroxyl radical. The mechanism of OH radical formation from TiO₂ under irradiation is explained by Bauer et al.³⁴ and is given in Scheme 1. This radical initiates the degradation of the polymer by hydrogen abstraction from the polymer chain. The products of photodegradation of PEO are aldehydes, formates, and the formation of hydroperoxide and hydroxyl groups. The evidences for the formation of these are obtained from IR and UV spectra.⁹ PAM is also susceptible to wide range of photodegradative processes by OH radicals, resulting in the introduction of new functional groups like OH and double bonds in the molecule.³⁵ In this study, the evidence for the formation of carbonyl group can be seen from UV spectra (Fig. 2) for both PEO and PAM. New absorption peaks can be seen between 250 and 300 nm corresponding to the absorption of aldehydes and ketones.

PEO is more susceptible to photodegradation and degrades at a faster rate than PAM. This is because PEO has C—O bond in its backbone that can be easily broken when compared with C—C bond in PAM. Based on the aforementioned observations, the mechanism of degradation can be deduced as given in Scheme 1.

The degradation of PEO and PAM were carried out without catalyst, Degussa P-25 and with CSN-TiO₂ catalyst, and with lamps of two different power (125 and 80 W). The random mode of chain scission exhibited by both the polymers in solution is evident from the linear variation of (M_{n0}/M_n) with time [Fig. 3(a)–(c)]. The rate coefficients k_d



a) for PEO

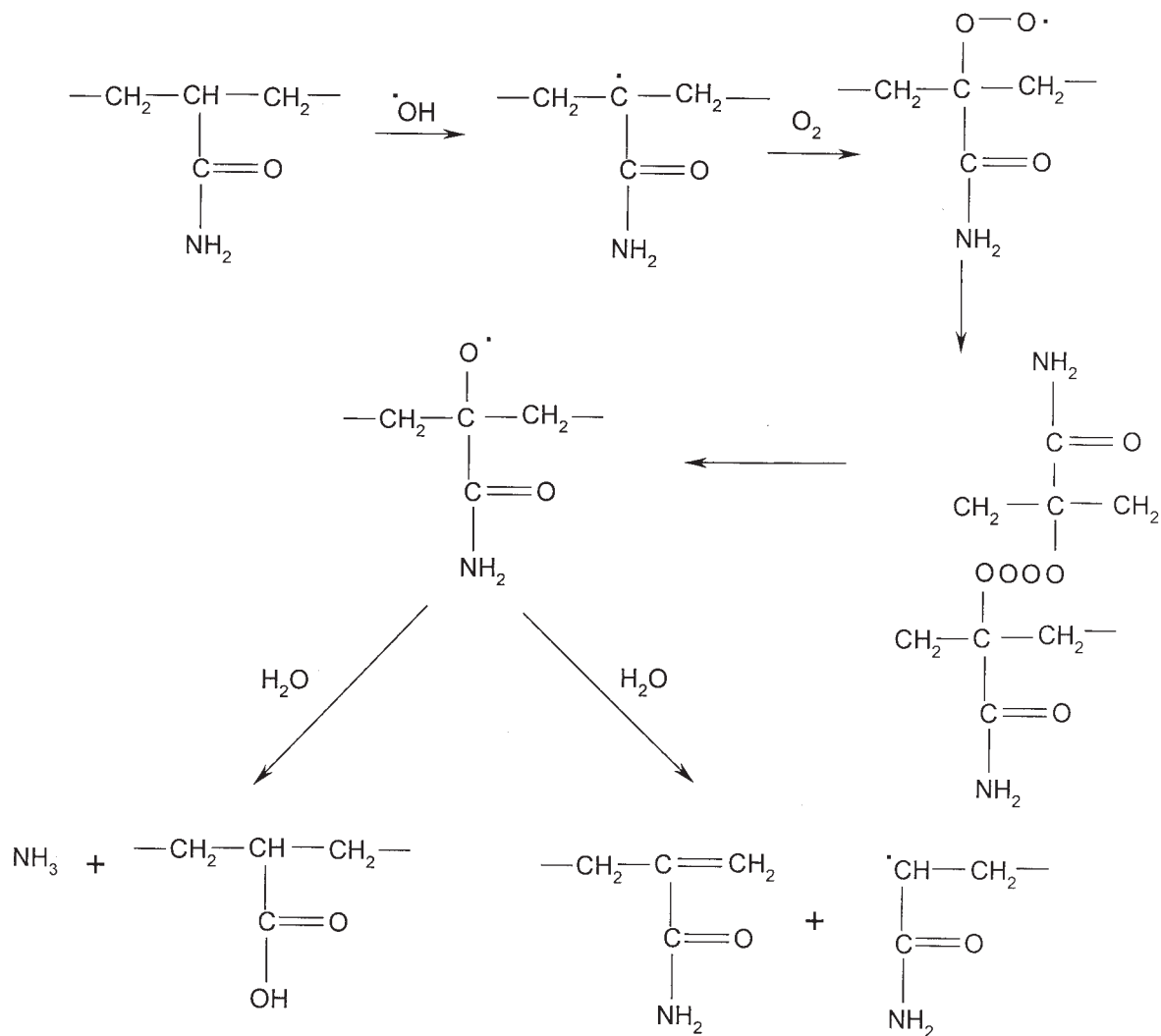


Scheme 1 Degradation mechanism for PEO and PAM in the presence of TiO_2 under UV irradiation.

(10^{-7} mol/g/min) obtained from the slope of the regressed lines are 0.60, 1.14, and 3.47 for the degradation of PEO without catalyst, with Degussa P-25 and CSN- TiO_2 , respectively, when 125 W lamp was used. This indicates that the presence of Degussa P-25 nearly doubles the noncatalytic reaction rate,

while the presence of CSN- TiO_2 increases the noncatalytic reaction rate by nearly six times. However, when an 80 W lamp was used for the photocatalytic degradation of PEO, the rate coefficients k_d (10^{-7} mol/g/min) are 0.30, 0.44, and 1.03 for degradation without catalyst, with Degussa P-25, and CSN- TiO_2 ,

b) for PAM



Scheme 1 (Continued)

respectively. This indicates that the presence of Degussa P-25 increased the noncatalytic reaction rate by nearly 50%, while the presence of CSN-TiO₂ increased the noncatalytic reaction rate by about 200%. One can also compare the degradation of PEO that results by employing lamps of different power. Comparing the degradation of PEO with the two lamps indicates that the degradation without catalyst doubles, while the degradation with CSN-TiO₂ increases by nearly 3.4 times when PEO is degraded with the lamp of higher power (125 W) compared with the case when PEO is degraded with the lamp of lower power (80 W).

The degradation rate coefficients k_d (10^{-7} mol/g min) are 0.52, 0.62, and 2.28 for the degradation of PAM without catalyst, with Degussa P-25, and CSN-TiO₂, respectively, when 125 W lamp was used. This shows that Degussa P-25 increases the degradation rate by nearly 20%, while CSN-TiO₂ increases the degradation rate by nearly five times when compared with the noncatalytic degradation rates. No degradation of PAM was observed when a lamp of 80 W was used, indicating that there is a minimum threshold intensity required for initiation of degradation of the polymer. Although the rate of degradation of organic compounds³⁶ and photopolymer-

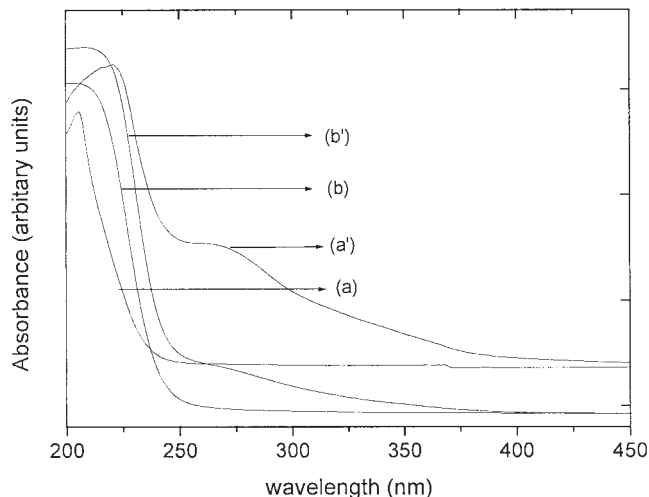


Figure 2 UV-visible absorption spectra for undegraded and degraded PEO and PAM. (a): PEO undegraded, (a'): PEO degraded for 3 h with 2 g/L TiO_2 , (b): PAM undegraded, and (b'): PAM degraded for 3 h with 2 g/L TiO_2 .

ization³⁷ varies to the power of half of the intensity, there is a minimum intensity below which no reaction occurs.³⁷

The influence of the catalyst concentration on the degradation rate coefficient for the degradation of PEO and PAM was investigated with a 125 W lamp and is shown in Figure 4. As expected, the degradation rate increases with catalyst concentration initially and then gradually seems to attain saturation at higher catalyst concentrations. However, a catalyst concentration of 2 g/L is ideal for studying the degradation, since the rate of degradation is comparable with rates at higher concentrations and also the separation of catalyst from the polymer solution is easier at lower concentrations.

CONCLUSIONS

The photodegradation of PEO and PAM was investigated with CSN- TiO_2 catalyst and commercial Degussa P-25 catalyst. The studies were also done at two different lamp powers of 125 and 80 W. The rate coefficient for the degradation process was determined from continuous distribution kinetics. Greater degradation occurred at higher lamp power for PEO, whereas no degradation occurred at lower lamp power for PAM, indicating that a minimum threshold of light intensity is necessary for initiating the degradation process. An enhanced degradation of the polymers was observed with CSN- TiO_2 catalyst compared with the commercial catalyst. The enhanced degradation rate by CSN- TiO_2 is due to its nano-size, high surface area, and the presence of large number of hydroxyl groups on the surface.

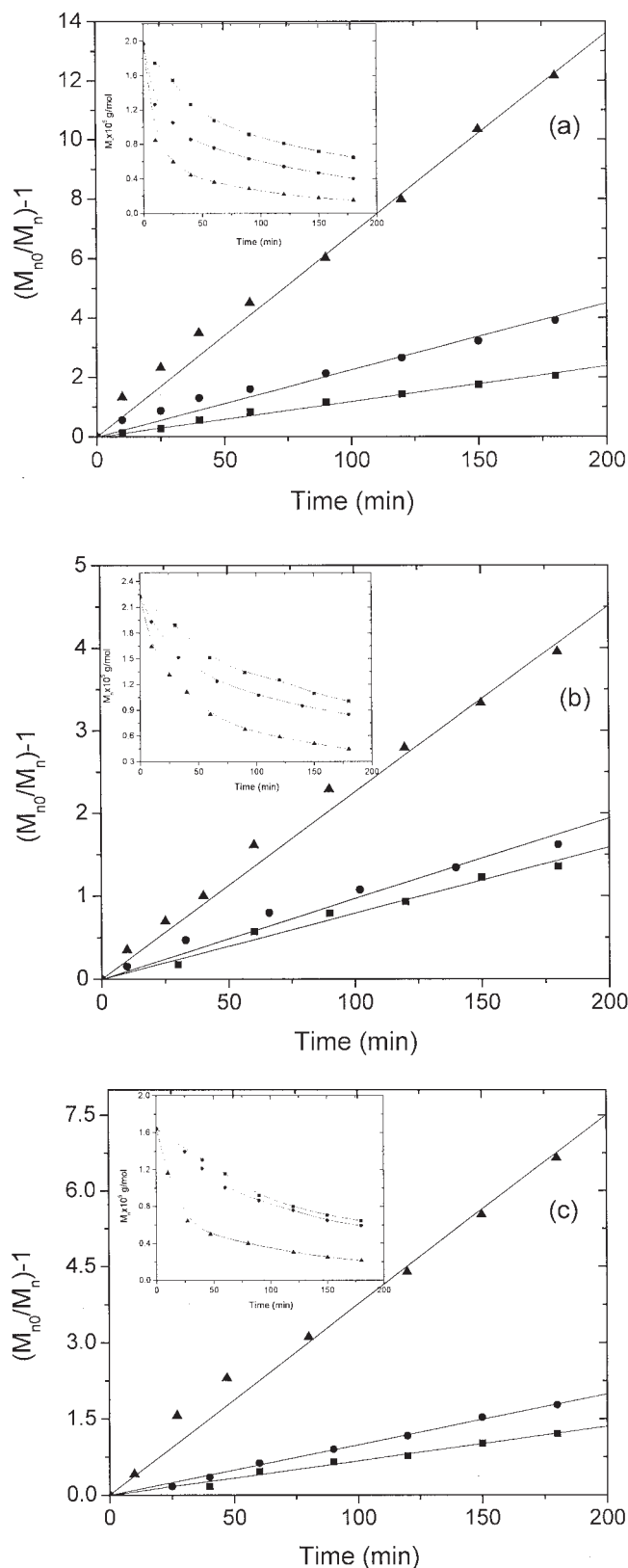


Figure 3 Variation of $[(M_{n0}/M_n) - 1]$ with reaction time using (a) 125 W lamp for PEO (b) 80 W lamp for PEO (c) 125 W lamp for PAM. ■: without catalyst, ●: with Degussa P-25, and ▲: with CSN- TiO_2 . Inset: variation of number average molecular weight with time.

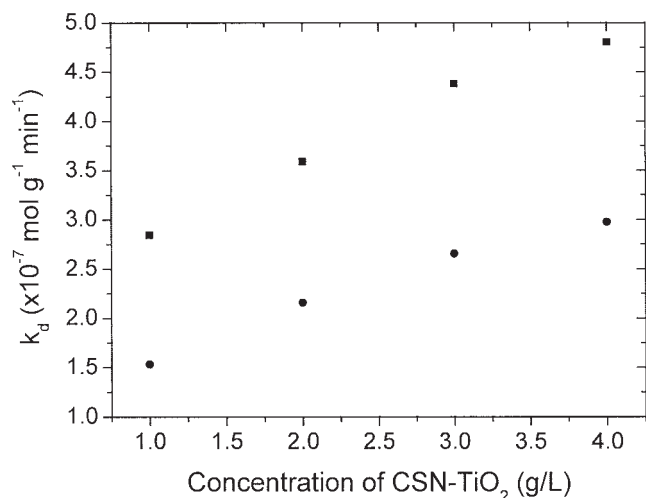


Figure 4 Variation of the degradation rate coefficient with concentration of CSN-TiO₂ catalyst. ■: PEO and ●: PAM.

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