ARI The Bulletin of the Istanbul Technical University VOLUME 53, NUMBER 1
Communicated by Bedia Erim Berker

Absolute, Online Monitoring of UV Initiated Bulk Polymerization of Methyl Methacrylate

Huceste Çatalgil-Giz and Ahmet Giz
Faculty of Sciences and Letters, Istanbul Technical University, 34469 Istanbul, Turkey
Alina Alb
Department of Physics, Tulane University, New Orleans, Louisiana 70118, U.S.A
(Received 18 October 2002)

A recently developed automatic, continuous, online monitoring technique was used to follow bulk photo-polymerization of methyl methacrylate without chromatographic columns. The technique furnishes the monomer conversion, reduced viscosity and the weight average polymer mass M_w as functions of time. Cross correlation of these quantities were also obtained.

Keywords: Photo-polymerization, online monitoring, polymerization.

1. Introduction

Florenzano et al. [1] have recently introduced a technique for continuous, absolute, online monitoring of polymerization reactions. The method furnishes the time dependent signature of cumulative weight average mass M_w, reduced viscosity η_r and the monomer conversion. More recently, several approaches have been taken to determine the evolution of the polydispersity during online monitoring [2]. On-line monitoring technique has been applied to the solution polymerization of acrylamide, solution copolymerization of styrene with methyl methacrylate, and step polymerization, and detailed investigations were published [3, 4, 5].

Ultraviolet (UV) initiated polymerization has many practical advantages. The rate can be controllcd, spatially and tcmporally, by controlling the light source [6]. This property is especially important in the printing and coating industries and has led to significant use of photo-initiated polymerization in these fields. Photo initiated polymerization can be performed with or without an additional initiator. Even when an additional initiator is used, the reaction temperature can be below its thermal dissociation temperature.

In this work the online monitoring method is applied to UV initiated bulk polymerization of methyl methacrylate using 2-2'azobis(isobutyronitrile), at room temperature. The reaction rates and molecular weight evolutions were monitored. In one case the UV irradiation was started at the time initiator was added and in the other case the monomer was exposed to UV for 30 mins before initiator was added.

2. Materials and Methods

2.1. Materials

Methyl methacrylate (MMA, Aldrich) was freed from inhibitor by washing in 5% sodium hydroxide solution, dried over calcium sulfate and fractionally distilled and stored in a fridge. The initiator, 2-2'azobis(izobutyronitrile) AIBN, (Aldrich), and the carrier solvent, butyl acetate (Aldrich) were used as received.

2.2. Online Monitoring of Polymerization Reactions

The continuous, absolute, online monitoring technique was described in detail in Ref. [3] and the supplement to that article contains additional details. It uses automatic, continuous withdrawal of a small stream of reactor solution, which is continuously mixed with a pure solvent from a reservoir (carrier solvent), in order to produce a very dilute polymer solution, on which useful light scattering and viscometric measurements can be made.

An ISCO 2360 Programmable Mixer was used to continuously withdraw nominal, preset percentages from the reactor and solvent reservoir, set at 4% and 96%, respectively. The flow rate was 2ml/min, so that about 5ml of reactor solution was consumed during the course of a typical reaction. As the viscosity of the medium increases

during the reaction the mixer pump cannot maintain the nominal percentage throughout the reaction and the pump efficiency decreases. For this reason the actual concentrations were determined as described below.

The diluted solution was continuously pumped through a detector train consisting of 1) a home-built, seven angle absolute light scattering intensity monitor (time dependent static light scattering, TDSLS), details of which have been recently published [7], 2) a home built, single capillary viscometer, which has also been described in detail [8], 3) a Shimadzu SPD-10AV Ultraviolet (UV) absorption spectrophotometer, and 4) a Waters 410 refractive index (RI) detector. The UV detector, with a 1 cm pathlength cell monitoring UV absorption at 280 and 285 nm, followed the disappearance of the C=C double bond in the monomer, during polymerization. As the refractive index increments of the monomer and its associated polymer are similar (but not equal) the RI detector provided total polymer and monomer concentration in the detector stream. Together, these two detectors yield the instantaneous concentration of polymer and monomer in the detector stream as long as the refractive index increment dn/dc is known for both monomer and polymer by the equations,

$$c_m(dn/dc)_m + c_p(dn/dc)_p = \Delta n \quad (1)$$

$$c_m(d\mathrm{UV}/dc)_m + c_p(d\mathrm{UV}/dc)_p = \Delta(\mathrm{UV\ volts}) \quad (2)$$

$$c_m + c_p = f c_0 \quad (3)$$

Here Δn is the refractive index increment between the pure solvent and the diluted reaction solution. Similarly Δ(UV volts) is the difference of the voltages measured by the UV photometric detector when pure solvent and diluted reaction mixture are passing through it. The pump efficiency factor f is the actual fraction being withdrawn from the reactor. The concentrations c_m and c_p are the monomer and polymer concentrations in the diluted mixture going through the detector train and c_0 is the initial concentration in the reaction vessel.

The dn/dc and $d\mathrm{UV}/dc$ values of the monomer and the polymer, obtained in preliminary experiments, are given in Table 1. In conjunction with the polymer concentration c_p, determined this way, the TDSLS monitor allows computation of absolute M_w and $\langle S^2\rangle_z$, using the well-known

Table 1
dn/dc and $d\mathrm{UV}/dc$ values of materials

	dn/dc	$d\mathrm{UV}/dc$ (280 nm)
MMA	0.0169	6
PMMA	0.0882	3.16
AIBN	0.0414	0.788

Zimm approximation [9], valid for $q^2\langle S^2\rangle_z \ll 1$,

$$\frac{Kc_p}{I(q,cp)} = \frac{1}{M_w}\left(1 + \frac{q^2\langle S^2\rangle_z}{3}\right) + 2A_2c_p \quad (4)$$

where $I(q, c_p)$ is the excess Rayleigh scattering ratio (total scattering of polymer solution, minus solvent scattering), and K is an optical constant, given for vertically polarized incident light by,

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A\lambda^4} \quad (5)$$

IIere n is the solvent index of refraction, λ is the vacuum wavelength of the incident light, and q is the scattering wave-vector $q = (4p_n/\lambda)\sin(\theta/2)$, and θ is the scattering angle.

A_2 was determined independently in separate Zimm plot measurements of final products of different M_w. It was found to be 5.97x10^{-4} cm^3-mole/g^2 $\pm$ 2.8% for PMMA. Since the molecular weight is low in this case, (approximately 50.000), the A_2 correction was really small and had negligible effect on the molecular weight measurements.

The viscometer was a single capillary mounted via T-connectors to a Validyne Engineering differential pressure transducer. The voltage output of the transducer is proportional to the pressure drop across the capillary, which in turn is proportional to total solution viscosity, via Poisseuille's law

$$\eta = \frac{\pi\ R^4 P}{8LQ} \quad (6)$$

where Q is the flow rate through the capillary (in cm^3/s). Total solution viscosity is

$$\eta = \eta_s\left[1 + [\eta] + k_p[\eta]^2 c_p^2\right] \quad (7)$$

where η_s is the pure solvent viscosity, $[\eta]$ is the intrinsic viscosity of the polymer, and k_p is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers [10]. The intrinsic viscosity is the extrapolation to zero concentration and

Table 2
Conditions for the UV initiated bulk MMA polymerization

Reaction	Monomer (g)	AIBN (g)	Temp, °C	mon. suction started (s)	initiator added (s)
06	10.0217	0.5014	25	227	1218
04	10.0186	0.5015	25	283	1283

zero shear rate of the reduced viscosity η_r. η_r can be computed directly from the voltage of a single capillary viscometer at every point in time t, without need of an instrumental calibration factor, in terms of the viscometer baseline voltage V_b and the concentration at point t, $c_p(t)$:

$$\eta_r(t) = \frac{V(t) - V_b}{c_p(t)\, V_b} \tag{8}$$

The average shear rate is about 860s^{-1} for $Q = 1$ ml/minute and $R = 0.0254$ cm. Shear effects diminish at low polymer concentrations.

2.3. Polymerization Reactions

In the polymerization reactions bulk monomer was placed in a small cylindrical tube (20 ml) and purged for 30 minutes by N_2 bubbling. Bubbling was continued throughout the reaction. The reaction tube was irradiated by a Xe lamp (220 - 1200 nm) . The solution was magnetically stirred during the reaction. The mixing pump was used to continuously withdraw nominally 4% of the liquid from the reaction vessel and mix this with 96% pure solvent from reservoir. The diluted solution flowed continuously through the detectors, which were stabilized before the initiator was added. After stabilization, AIBN, dissolved in a few milliliters of monomer was added to the reaction vessel. The reaction conditions are given in Table 2. Conversion of the monomer to polymer was followed with the decrease of UV absorbtion of the monomer during polymerization reactions. In preliminary experiments, performed to test for pure photo initiated polymerization of MMA without initiator, in this case no polymerization was observed. UV lamp in experiment 04 is turned on at the time of initiator addition and experiment 06 being irradiated since the beginning of 4% monomer suction.

3. Kinetics of polymerization

The mechanism of UV initiated polymerization of MMA is as follows:

$$\begin{aligned} I_2 &\xrightarrow{\text{UV}} 2R^* \\ R^* + M &\longrightarrow M_1^* \\ M_n^* + M &\longrightarrow M_{n+1}^* \\ M_n^* + M_m^* &\longrightarrow P_n + P_m \end{aligned}$$

Here I_2, R^*, M_1^*, M_n^* and P_n are undissociated initiator, initiator radical, primary radical, macro radical and dead polymer respectively.

AIBN absorption spectrum has a maximum near 360 nm. Its photolysis generates free radicals at room temperature and below, and it is frequently used in UV initiated polymerization. The decomposition reaction is similar to thermal decomposition. The photo dissociation rate is given by

$$R_p = k_{dp}\,[I_2]\,\iota \tag{9}$$

Here ι is the local intensity of the UV radiation and k_{dp} is the rate constant for photodissociation. The overall rate is the integral of this quantity over the reaction vessel. When the vessel is well mixed it can be assumed that $[I_2]$ is constant throughout but as the vessel is illuminated only from the top surface, ι is a function of depth. Two approximations are commonly used. If the UV absorbtion is low then the intensity is constant and the overall dissociation rate is also proportional to the initiator concentration. If on the other hand the UV absorbtion due to the initiator is high enough then almost all of the photons get absorbed so that the total initiation rate depends solely on the UV intensity and is independent of the initiator concentration [5].

The initiator decay is then given either by the first order process,

$$[I_2] = [I_2]_0 \exp(-k_{dp}\,\iota t) \tag{10}$$

or the zeroth order process

$$[I_2] = [I_2]_0(1 - \alpha t) \tag{11}$$

where α is a rate constant that depends on the intensity of the UV source. The concentration of the radicals $[R^*]$ which then form, satisfies,

$$d[R^*]/dt = 2Fk_{dp}\,\iota[I_2] - k_t[R^*]^2 \tag{12}$$

where F is the fraction of radicals that lead to chain propagation. The variation of ι within the reactor depends on the absorbtion coefficients of the initiator, monomer and solvent. In this case both MMA and AIBN are strong UV absorbers and there is no solvent. Under these conditions almost all of the UV photons are absorbed but there is competition between the AIBN and monomer for the photons. Here the termination constant adheres to the definition used by Dotson et al. [11] and Bamford [12] and is twice the value used by Odian [6]. The rate equation for monomer concentration is,

$$d[M]/dt =$$

$$-2F\,k_{dp}\,\iota[I_2] - k_p[R^*]\,[M] \sim -k_p[R^*]\,[M] \tag{13}$$

The quasi-steady state approximation states that

$$d[R^*]/dt \sim 0 \tag{14}$$

Under this approximation, radical concentrations are given by

$$0 = d[R^*]/dt = 2F\,k_{dp}\,\iota[I_2] - k_t[R^*]^2 \tag{15}$$

which leads to,

$$[R^*] = (2F\,k_{dp}\,\iota[I_2]/k_t)^{1/2} \tag{16}$$

Monomer then disappears in a first order process

$$[M] = [M]_0 e^{-\kappa t} \tag{17}$$

where the overall rate constant κ is given by

$$\kappa = k_p\,(2F\,k_{dp}\,\iota[I_2]/k_t)^{1/2} \tag{18}$$

In the case that irradiation had started with initiator addition, a long induction period was observed. Starting the irradiation, before initiator addition, remarkably decreased the induction period. In 6000 seconds 12-16% conversion was obtained with 5% AIBN at room temperature and the molecular weight levelled off at around 35.000.

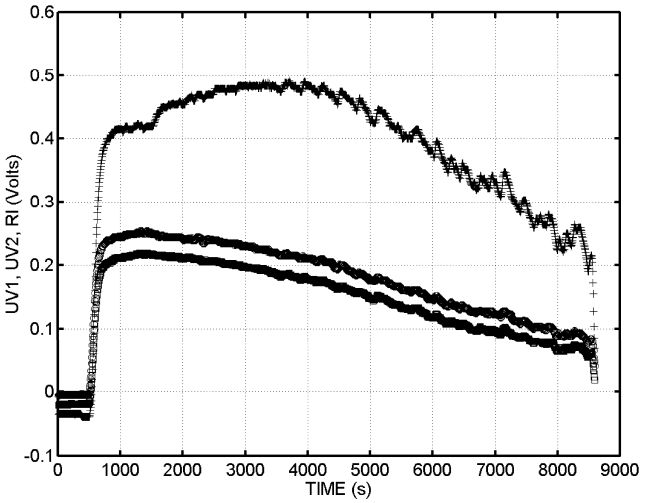

Figure 1. Raw data for experiment 04. RI, UV (280nm) and UV2 (285nm) (from top to bottom) signals.

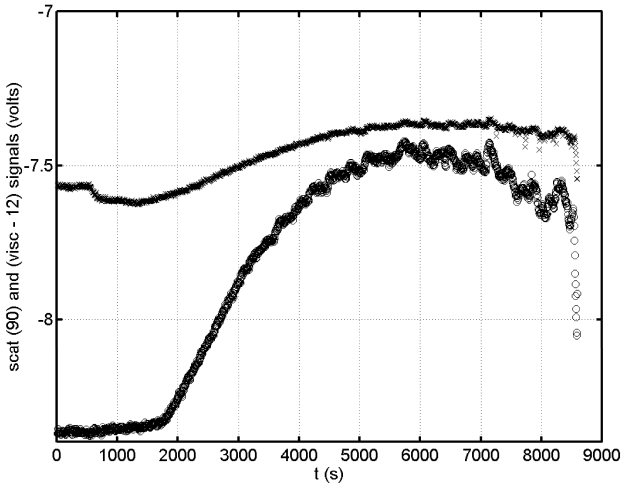

Figure 2. Raw data for experiment 04. Viscosity(top) and light scattering at 90° (bottom) signals.

4. Results and Discussion

In preliminary experiments with no AIBN, the system had not polymerized at all at the end of two hours of irradiation.

Table 2 is a summary of polymerization conditions. Fig. 1 shows typical raw data signals for a UV initiated MMA polymerization (Table 2, reaction 04) UV (280 nm), UV2 (285 nm) and RI signals are given as voltages. Fig. 2 shows light scattering signal measured at $\theta = 90°$ and viscosity signal. Significant features in Fig. 1 and Fig. 2 include the stable detector plateau when pure solvent is being pumped at 283sec which appeared at the detectors around 536sec, the rise of the RI and UV signals when pure monomer is pumped prior to addition of initiator, and the point at which initiator is injected at 1283 seconds. The segments corresponding to pure solvent, 4% reaction solution, and the post-reaction flush with solvent are visible, as well as the point where initiator was added. The lag time between adding initiator and observing its effect on the detectors is 250s. As the reaction proceeds, the UV signal decreases, showing the conversion of monomer to polymer, and in Fig. 2, the light scattering and viscometer signals increase as polymer is produced. A dip in the RI curve in Fig. 1 indicates that the reactor liquid is becoming more viscous and the mixing pump cannot pull the preset percentage. This does not hamper the data analysis, since the polymer concentration is being continuously monitored and M_w and other quantities can be computed. In this experiment the drop in pump efficiency dominated the RI behavior, which otherwise would have increased as polymer was produced, if pump efficiency remained the same, since dn/dc of the polymer is greater than that of the monomer.

Fig. 3 shows monomer conversion f ($f = 1 - [M]/[M]_0$) , vs. time. The UV lamp in experiment 04 is turned on at the time of initiator addition. A long induction period is seen in this experiment. Since the inhibitor is already removed during monomer preperation, as described above, the induction period is due to impurities, mostly oxygen dissolved in the monomer.

In order to test if this inhibition action was also a factor in preventing the polymerization in the preliminary experiments with no initator, the experiment 06 was irradiated for 30mins before initiator addition. In this experiment there was

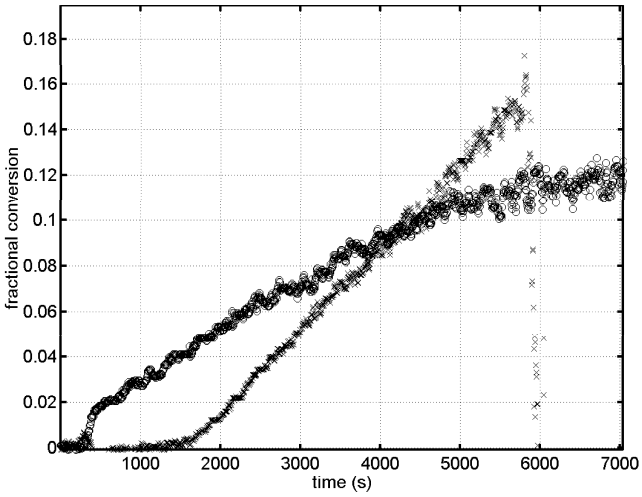

Figure 3. Monomer conversion f vs. time

no significant induction period. The simplest explanation of this behavior is: irradiation before the addition of the initiator in experiment 06 causes some monomers to be initiated, these cannot grow to become polymers because of the inhibition action, however, this process also depletes the inhibiting oxygen so that when the initiator is added the already depleted oxygen is swept out by the abundant radicals produced by the initiator and the reaction begins with no detectable induction period.

The curve for experiment 04 can be treated approximately either as first order, of the form,

$$f(t) = 1 - e^{-\kappa(t-t_i)} \tag{19}$$

or zeroth order, of the form,

$$f(t) = \kappa(t - t_i) \tag{20}$$

where κ is the first order composite decay rate constant defined by Eq. (16), and t_i is an induction period. The best-fit values are: $\kappa^{-1} = 27500$s and 25300s for the zeroth and first order fits respectively and $t_i = 1590$s and 1660s, for the zeroth and first order fits. The R values for the fits, 0.99719 and 0.99694 indicate that the low final conversion (16%) does not allow clear distinction between the two possibilities. The experiment 06 however deviates from both zeroth and first order kinetics even at the low conversion ($\sim 10\%$). The differences in the kinetic behaviors are due to their irradiation schemes. The slowing

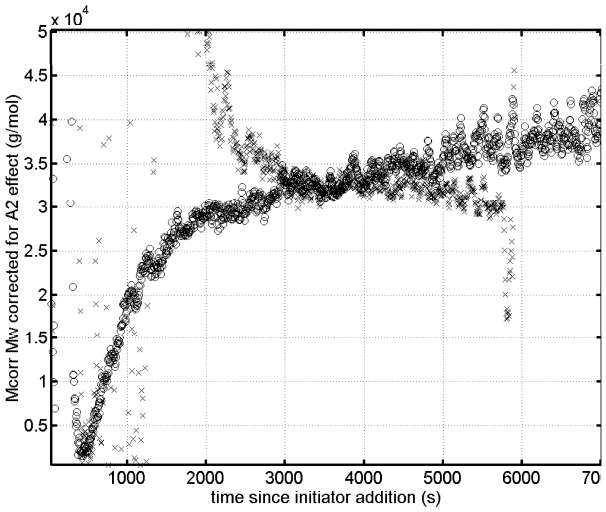

Figure 4. Molecular weight (including A_2 correction) versus time for 06 and 04.

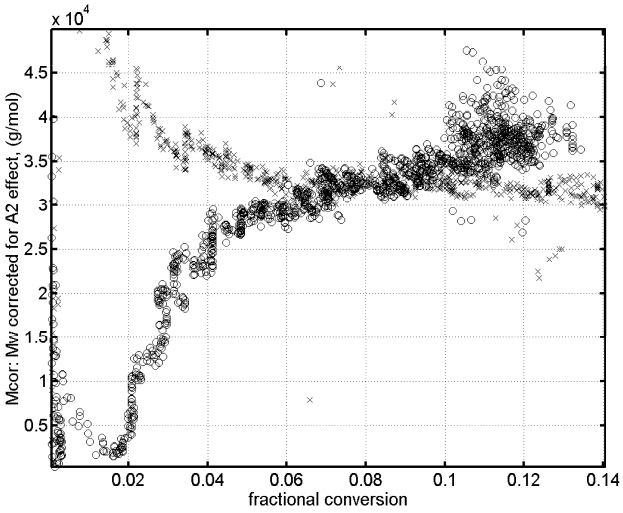

Figure 5. Molecular weight (including A_2 correction) versus conversion for both reactions.

down of the reaction in experiment 06 indicates that the initiator is more rapidly used in this case.

Corrected (for A_2 effects) M_w's versus time and versus conversion f are given in Fig. 4 and Fig. 5 respectively for 04 and 06. Disregarding very early results when conversion is less than 3-4%; molecular weights are relatively constant at around 35 000-40 000 for both experiments. Reduced viscosity versus time plots are given in Fig. 6.

Further substantiation of the trends in Figs. 4 and 5 is seen in fig 7, where the online values of reduced viscosity are shown vs. f. The two independent detectors show the same qualitative behavior for η_r and M_w. Molecular weight and reduced viscosity values levels off after 5% conversion. The first portion of the plots are not that reliable due to measurement errors are high when the conversion very low in this region.

The results show that the polymerization rate approaches a steady value after an induction period, which is due to impurities like remaining dissolved oxygen. After the end of the induction period the reaction rate and the molecular weight were both nearly constant until the reaction was terminated at around 10-15% conversion.

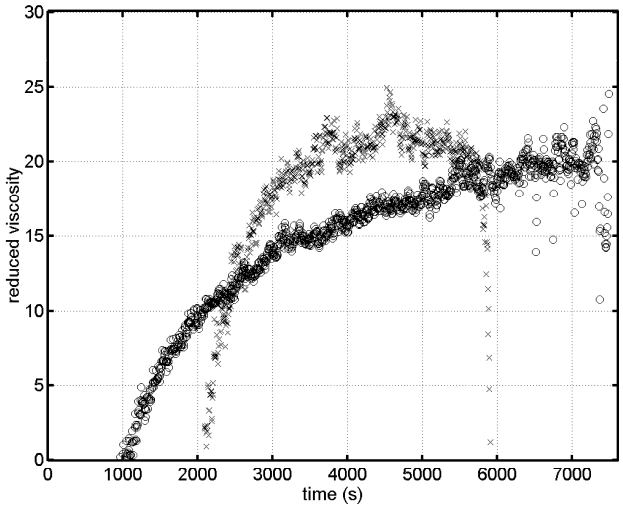

Figure 6. Reduced viscosity versus time.

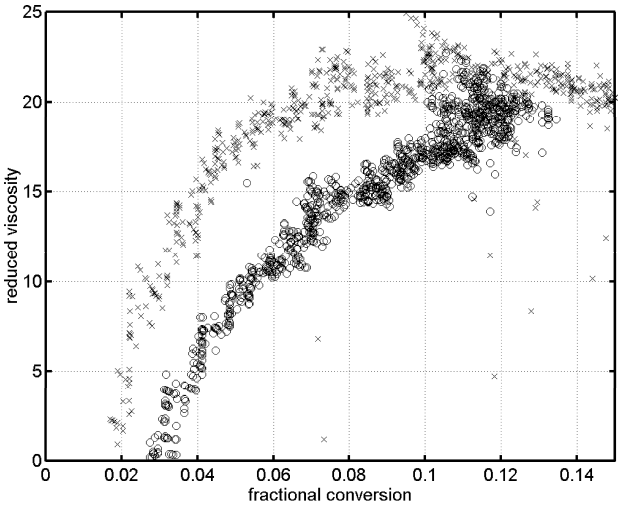

Figure 7. Reduced viscosity versus conversion.

5. Conclusions

The continuous, absolute online monitoring of bulk MMA polymerization has shown that no visible photo polymerization occurs under the conditions outlined here without initiator addition. However UV irradiation of the monomer, prior to the addition of the initiator, effects the polymerization kinetics considerably. With no pre-irradiation the there is an approximately 20min of induction period followed by polymerization at a nearly constant rate. At the rather low conversion of our experiment this result is consistent with either first order kinetics as described by the Eq. (16a) and the zeroth order kinetics of Eq. (16b).

Pre-irradiation of the monomer eliminated the induction period, however reaction kinetics were more complex as seen by the slowing down of the reaction beginning at about 5% conversion.

In both reactions, with and without pre irradiation, the M_ws were nearly constant at 30000 to 35000. This result is seen both in the light scattering and viscosity data. Note that results obtained at very low conversion (<3-4%) involve a division of a very small signal by a small polymer concentration, and for this reason are not as reliable as results obtained later in the reaction.

6. Acknowledgements

We express our thanks to Prof. Wayne Reed of Tulane University Physics Department, for allowing us full use of his laboratory and the monitoring system during these experiments. H. Çatalgil-Giz and A. Giz thank ITU Research Fund for support under projects 1673 and 1653 respectively and to TÜBİTAK for support under projects TBAG-U2(100T141) and TBAG-2174(102T060).

References

[1] F. H. Florenzano, R. Streliktzki, and W. F. Reed, Macromolecules **31**, 7226 (1998).
[2] W. F. Reed, Macromolecules **33**, 7165 (2000).
[3] A. Giz, H. Çatalgil-Giz, J.-L. Brousseau, A. M. Alb, and W.F. Reed, Macromolecules **34**, 1180 (2001).
[4] H. Çatalgil-Giz, A. Giz, A. Alb, A. Öncül-Koç, and W. F. Reed, Macromolecules **35**, 6557 (2002).
[5] H. Çatalgil-Giz, A. Giz, A. Alb, and W. F. Reed, J. Appl. Polym. Sci. **82**, 2070 (2001).
[6] G. Odian, Principles of Polymerization (3rd Ed., John Wiley & Sons, Inc. 1991).
[7] R. Strelitzki and W. F. Reed, J. Appl. Polym. Sci. **73**, 2359 (1999).
[8] D. P. Norwood and W. F. Reed, Int. J. Polym. Anal. Charact. **4**, 99 (1997).
[9] B.H. Zimm, J. Chem. Phys. **16**, 1093 (1948).
[10] M. L. Huggins, J. Am. Chem. Soc. **64**, 2716 (1942).
[11] N. A. Dotson, R. Galvan, R. L. Laurence, and M. Tirrel, Polymerization Process Modelling (VCH Pub., New York, 1996).
[12] C. H. Bamford, Encyclopedia of Polymer Science and Engineering (Interscience **13**, 708, J. Wiley & Sons, New York 1991)