

CHAPTER 10

DENSITY AND VISCOSITY AS REAL-TIME PROBES FOR THE PROGRESS OF HIGH-PRESSURE POLYMERIZATION: POLYMERIZATION OF METHYL METHACRYLATE IN ACETONE

Density and viscosity can be used as real-time probes to follow the progress of polymerization reactions. The basic premise is linked to the fact that viscosity increases with polymerization and polymerization leads to a reduction in volume (or increase in density). Effect of viscosity on reducing the rate of termination and its consequences with respect to increased rate of polymerization that may lead to autoacceleration (otherwise known as the “gel effect”) is well recognized in ambient pressure polymerizations (Odian, 1991). We have therefore adopted our unique capabilities to measure both the density and the viscosity to explore the progress of a polymerization reaction. We have investigated the polymerization of methyl methacrylate in acetone at high pressures as a case study. To our knowledge, this is the first time that real time changes in viscosity of polymerizing systems at high pressures are being reported.

10.1 Introduction

Polymerization at high pressures in dense or supercritical fluids is of both scientific and technological importance. This is because high pressure influences not only the

polymerization rate and equilibrium conditions (Ogo, 1984; Beasley, 1989), but also because the use of supercritical fluids provide new opportunities for developing environmentally-friendly and tunable processes for polymer formation and modifications (Canelas and DeSimone, 1997; Kiran, 1994; Ajzenberg et. al., 2000).

Among the supercritical fluids, carbon dioxide as a polymerization medium has received by far the greatest attention (Canelas and de Simone, 1997; Wood et. al., 2000). Majority of polymerizations in carbon dioxide are carried out using stabilizers which are typically fluorocopolymers that contain segments that are compatible with the polymer and carbon dioxide (Canelas and de Simone, 1997; Sarbu et. al., 2000). Recent publications describe the dispersion polymerization of methyl methacrylate in supercritical carbon dioxide using a range of stabilizers (Giles et. al., 2000; 2001).

There have been also studies in which polymerizations have been carried out in the absence of stabilizers. For example, Buback and coworkers have investigated the high-pressure free-radical polymerization of styrene in carbon dioxide (Beuermann et. al., 2002), and more recently, Yeo and Kiran reported on the precipitation copolymerization of acrylonitrile with methyl methacrylate or 2-chlorostyrene in supercritical CO₂ (Yeo and Kiran, 2004).

Kinetics of polymerization at high pressures has been of particular interest. Due to complications associated with sampling, almost invariably indirect methods are used in these investigations. Buback and coworkers measured propagation coefficient for homopolymerization of styrene in supercritical CO₂ (Beuermann et. al., 2002) and

investigated the termination kinetics of methyl acrylate and dodecyl acrylate free-radical homopolymerizations at high pressure using pulsed-laser techniques (Buback et. al., 2002). Howdle and coworkers monitored precipitation polymerization of vinylidene fluoride (Liu et. al., 2005) and dispersion polymerization of methyl methacrylate (Wang et. al., 2003b) in CO₂ using a high-pressure calorimeter. Johnston *et al* investigated the polymer particle formation from the dispersion polymerization of methyl methacrylate in CO₂ with siloxane-based macromonomer as stabilizer using turbidimetry (O'Neill et. al., 1998).

In this chapter we present the use of density and viscosity as probes of the progress of polymerization since viscosity increases with polymerization, and polymerization leads, in general, to a reduction in volume. The direct measurement of viscosity during polymerization can also be of value in prevention of autoacceleration. Polymerization systems in which viscosity increase is large may display autoacceleration (O'dian, 1991). In polymerization, especially in bulk polymerizations, viscosity of a polymerization mixture increases dramatically with the formation of polymer and with an increase in its molecular weight. Viscosity greatly influences (reduces) the rate of termination in free-radical polymerization and consequently the rate of polymerization (increase). Termination is a mass-transfer controlled step, and in systems where viscosity increase is large and heat dissipation is slowed down, rate of polymerization is increased due to increased temperature and autoacceleration sets in.

Even though viscosity is of such importance, to our knowledge it has not been used in the past to follow the progress of high-pressure polymerizations. The reason may be partly due to

the challenges associated with the in-situ measurement of viscosity at high pressures. This is a unique capability that we have in our laboratory and have illustrated in the previous chapters its use in determining the properties of fluid mixtures and polymer solutions. We now report on the use of density and viscosity measurements in monitoring the progress of free-radical polymerization of methyl methacrylate (MMA) in acetone at 343 K at pressures in the range from 7 to 42 MPa.

10.2 Experimental

The polymerization reactions were all carried out in the high-pressure viscometer, which has been described in Chapter 4. This viscometer not only permits measurement of the viscosity but also provides information on the phase state and the density of the solutions. For each polymerization run, the monomer (MMA) and initiator (AIBN) with known amounts were loaded through the top loading port (TLP) before closing the viscometer. The solvent (acetone) was transferred from a separate solvent transfer vessel into the viscometer by a high-pressure liquid pump through the solvent line (SL). The amount of acetone charged was determined by the change in the total mass of the acetone transfer vessel before and after charging the viscometer. The mixing of the reaction mixture is achieved with the aid of a stirring bar activated by the electromagnetic stirrer (EMS) at the bottom of the viscometer and a circulation pump. Then, the temperature was adjusted to the target temperature (which in the present study was 343 K) by turning on the heating of the enclosure housing the viscometer parts. Once the desired temperature is reached, the pressure is adjusted by changing the position of the piston (PI) with the aid of a pressure generator. During the

polymerizations, the pressure would decrease because of the volume reduction of the reactant mixtures with the formation of polymer. To maintain constant pressure, the piston position was adjusted with the pressure generator. The density of the reaction mixture in the viscometer was determined at any time from the initial mass loading of the monomer (MMA), initiator (AIBN) and the solvent (acetone) used as the polymerization medium, and the inner volume of the viscometer at that particular time which is determined from the position of a movable piston. For viscosity measurements, the sinker (S) is brought to the top of the fall-tube (FT) by a pull up electromagnet (PM). When the sinker is released it falls and passes through a set (3) of linear variable differential transformer coils (LVDTs). The signal voltage readings (V) from each coil are processed to generate a fall distance (D) versus time plots, from which the terminal velocity of the sinker V_t is determined. Then the viscosity is calculated from the density of the sinker ρ_s (known) and the density of the solution ρ_f (measured).

10.3 Polymerization conditions and product recovery

The polymerizations were conducted at 343 K and at 7, 14, 21, 28, 35 and 42 MPa. The composition of initial reaction mixture was fixed at 10 wt % MMA and 90 wt % acetone with 0.04 wt % AIBN as initiator. The temperature is a typical temperature used in polymerizations using AIBN as initiator. The half life of AIBN at 343 is reported as 4.8 hrs compared to 74 hrs at 323K and 7.2 min at 373K (Odián, 1981). The polymerization reactions were carried out for 10 hrs. Then, the viscometer content was discharged at high pressure, and the viscometer was then washed with acetone at 343 K and 14 MPa to remove

any residual fractions that are not recovered during the discharge. The discharge and the washout were collected, the solvent was evaporated at ambient conditions and then further dried under vacuum for 72 hrs to remove any residual acetone and monomer, and obtain the final polymer sample.

The yields were obtained from the ratios of amount of PMMA recovered to MMA in the initial reaction mixtures. They were around 80 % for polymerization at pressures in the range from 7 to 21 MPa, and were around 90 % for polymerizations at higher pressures. Molecular weights were determined by gel permeation chromatography using polystyrene standards and THF as solvent. The molecular weights were around $M_w = 24,000$ with polydispersities in the range 1.5-1.6 for polymerizations at pressures up to 21 MPa, The molecular weights essentially doubled to 42,000 for polymerizations at higher pressures with polydispersities in the range 1.4-1.5. Higher pressure is known to lead to suppression of the termination step of the free-radical polymerization and often lead to higher molecular weights and narrower molecular weight distributions (Kiran and Saraf, 1990). The yield and molecular weight information are given in Table 10.1. The GPC tests for PMMA samples formed at 28 and 35 MPa are shown in Figure 10.1. The polymer samples are unimodal, which is consistent with the homogeneous polymerization conditions.

10.4 Variations of density and viscosity with time during polymerization

The progress of polymerization was monitored by measuring the temperature, pressure, density and viscosity of the reaction mixture every 30 minutes during polymerizations which

were carried out for 10 hours. Figures 10.2 and 10.3 show these changes during the polymerizations conducted at two different pressures, 21 MPa and 42 MPa, respectively. The figures show that temperature reached the target value of 343 K within about 100 min. As indicated earlier, the pressure was continually adjusted to compensate for the volume reduction as a result of polymerization and thus to maintain the system at the initial selected pressure for the experiment, i.e., in these figures, the pressure was maintained at 21 MPa (Figure 10.2) or 42 MPa (Figure 10.3).

Figures 10.4 and 10.5 compare the variation of density and viscosity with time during these polymerizations conducted at different pressures. As illustrated in Figure 10.4, during the time interval from 100-600 min, the density increases with time at all polymerization pressures. At a given polymerization time, densities are higher for higher polymerization pressures. In these figures the increase in density appears smaller than it actually is due to the compression of the density scale used to capture both the initial and later stage of polymerization at different pressures. Figure 10.6 shows the variation of density in an enlarged scale for polymerization conducted at different pressures. As shown in this figure, at any given pressure, density is found to increase with polymerization time but at two different rates. At 7 MPa, the rate is $2.2 \times 10^{-5} \text{ g / (cm}^3 \text{ min)}$ in the time interval from 100 to 360 min, then it is reduced to $8.2 \times 10^{-6} \text{ g / (cm}^3 \text{ min)}$. At 21 MPa, the changing rates are, 2.2×10^{-5} and $11.7 \times 10^{-6} \text{ g / (cm}^3 \text{ min)}$, with the change occurring at around 240 min. At 14 MPa the change in rate is noted at 260 min. At higher pressure, the change in rate is observed at around 260 min, which remains the same for polymerizations conducted at 28, 35, and 42

MPa. The values at different pressures are given in Table 10.2. The kinetics is altered at different transition times depending upon the pressures of polymerizations.

Figure 10.5 shows the change of viscosity with time at different pressures. Similar to density, at a given pressure viscosity increases with polymerization time, and at a given polymerization time, viscosities are higher at higher pressures. Enlargement of the viscosity scale shows that similar to density, viscosity too increases at two different rates during polymerization. Figure 10.7 illustrates this for polymerization carried out at different pressures. At 14 MPa, the rate of change of viscosity is reduced after about 360 min polymerization time. The shift in the rate of change of viscosity is observed at shorter times with increasing pressure. It is observed around 420 min at 7 MPa, around 360 min at 14 MPa, and around 320 min at 21 MPa and higher pressures. Above 21 MPa, the time for transition appears to be the same which is similar to the change in density. It is interesting to note that the change in rate in viscosity occurs at longer transition times. The rate of change in viscosity and the different time domains at different pressures are also given in the Table 10.2.

Figure 10.8 show the rate of change of viscosity with pressure in the early and late stage of polymerizations. Viscosity changing rate in the initial time domain shows a clear increase with pressure from 5×10^{-4} to 1×10^{-3} mPa·s / min in going from 7 to 28 MPa after which it is essentially unchanged up to 42 MPa. In the end stage, the rates of change in viscosity are smaller than those in the initial stage at the same pressure.

With the formation of polymer, the reaction mixture, which is initially a binary mixture of monomer and solvent, becomes a ternary mixture constituting of the polymer plus the monomer and the solvent. The concentration and chain length of the polymer undergo a continual change (an increase) while the monomer concentration decreases during the course of polymerization. The polymer poly (methyl methacrylate) has higher density than that of the monomer methyl methacrylate, and thus the reaction mixture shows an increase in density with time. The formation of the polymer and the increases in polymer concentration and molecular weight contribute to the increase in viscosity.

10.5 Comparisons with density and viscosity of reference polymer solutions

In Chapter 6 (Liu and Kiran, 2006), we presented the density and viscosity data for acetone and for 10 wt % solutions of PMMA with different molecular weights ($M_w = 15 \text{ K}$ and 540 K) in acetone. We have compared the density and viscosity of the polymerization systems at the end of the polymerizations at different pressures, with the density and viscosity of the reference polymer solutions at the corresponding pressures. The comparisons are shown in Figures 10.9 and 10.10. Figure 10.9 shows that the density increases as expected with pressure for all the systems. Acetone shows the lowest density, while densities of the PMMA solutions for the known molecular weight samples showing the highest densities. The densities of the polymerization system are higher than that of the solvent acetone, but are distinctly lower than the densities of the reference polymer solutions. This may be a consequence of the presence of the unreacted monomer or oligomers in the polymerization system since the yields were in the 80-90 % range.

Figure 10.10 shows the variation of viscosity with pressure for the same systems. Viscosity increases with pressure for all systems as it should. The pressure sensitivity of viscosity is very low for acetone, essentially remaining unchanged at all pressures tested at this temperature. At any given pressure, the viscosities consistently increased in going from acetone to reference polymer solution with low-molecular weight ($M_w = 15$ K), to polymerization system, and to reference polymer solution with high-molecular weight ($M_w = 540$ K). The data suggests a molecular weight intermediate to the molecular weights of the reference PMMA samples. Indeed, the polymers produced in the present polymerization experiments had molecular weights in the range from 24 K - 42 K g/mol.

10.6 Assessment of the rate of change of monomer (MMA) concentration during polymerization from viscosity and density measurements

To assess the change in the monomer (MMA) or polymer (PMMA) concentration with time during polymerizations at different pressures, densities and viscosities of a series of PMMA solutions of known concentration in acetone or in mixtures of acetone + monomer (MMA) were measured at the same P/T conditions used for the polymerizations ($T = 343$ K; $P = 7, 14, 21, 28, 35, \text{ or } 42$ MPa). The PMMA sample with molecular weight of 15 K was used to prepare these solutions since the GPC test shows the molecular weights of the polymerization product PMMA samples are in the range of 22 – 47 K g/mol. The acetone concentration was kept at 90 wt %, and the MMA concentrations were varied from 2.5 to 5.0 or 7.5 wt %, with the difference being PMMA (15 K). However, in these measurements, the monomer MMA

was used without removing the inhibitor to prevent any polymerization during the measurements that were conducted at 343 K. The densities and viscosities of these solutions are shown in Figures 10.11 and 10.12, respectively. In these figures we have also included two additional data points. The 10 wt % data corresponds to the initial mixture density and viscosity of the polymerizing systems at a time corresponding to 120 min when polymerizations have not significantly proceeded. The low MMA concentration data at each pressure correspond to the MMA conversion in the polymerization systems at the end of the polymerization (corresponding to $t = 600$ min) or obtained from the yield determinations.

Even though all the measurements were conducted using the MMA monomer without removing the inhibitor, we still needed to assure that there is no PMMA formed during these measurements. The GPC tests were done on the 5 wt % MMA monomer (with and without inhibitor) solution in acetone, which had been kept in the viscometer at 343 K for 24 hours. The results were compared with the GPC results for the 5wt % solutions of PMMA ($M_w = 15$ K) and PMMA (540 K). The results are shown in Figure 10.13. The elution peaks of reference PMMA solutions are clearly displayed. A small peak is observed for the case where the inhibitor in the monomer had been removed. There is no detectable polymer peak for the case where the inhibitor had not been removed from the monomer, confirming that no polymerization had taken place.

By comparing the density and viscosity data shown in Figures 10.11 and 10.12 with the density and viscosity data in polymerization systems (Figures 10.4 and 10.6), we generated the variation of MMA concentration during polymerization. These are shown in Figures

10.14 and 10.15. The monomer concentration shows a clear decrease with the progress of polymerization in the both figures. Two regimes are displayed. The monomer depletion is initially relatively high and the rate reaches a lower plateau value after 400 min. Two variations from density and viscosity at 35 MPa are presented in the Figure 10.15 for comparison. Even though there are some differences, they are basically identical.

Documentation of the rate of monomer depletion as a function of time at different pressures gives the opportunity to evaluate the polymerization rate constant at different pressures.

The basic rate expression for free-radical polymerizations is given by

$$d[M]/dt = -k[M][I]^{1/2} \quad (\text{Eq. 10.1})$$

where k is a combined rate constant $k = k_p (k_d / k_t)^{1/2}$ that involves the rate constant for initiator decomposition, k_d , the rate constant for propagation, k_p , and the rate constant for the termination steps k_t (Odian, 1991). The term $[I]$ is the initiator concentration which is given by

$$[I] = [I_0] \exp(-k_d t) \quad (\text{Eq. 10.2})$$

When equation 10.2 is substituted into equation 10.1, one obtains

$$d[M]/dt = -k[I_0]^{1/2} \exp(-k_d t / 2) [M] \quad (\text{Eq. 10.3})$$

or

$$\ln[M] = \ln[M_0] - 2k/k_d [I_0]^{1/2} (1 - \exp(-k_d t / 2)) \quad (\text{Eq. 10.4})$$

or

$$\ln[M] = \ln[M_0] - 2k_p ([I_0] / k_t k_d)^{1/2} (1 - \exp(-k_d t / 2)) \quad (\text{Eq. 10.5})$$

This equation predicts an exponential decay in the monomer concentration with time. The general shape of the data in Figure 10.15 is consistent with this expectation.

One could fit the data to equation 10.5 and in principle determine k_p/k_t ratios if values for k_d for AIBN were available at different pressures and temperatures. In the absence of such information, in the present study, we instead employed a simpler approach and evaluated a first order apparent rate constant for the initial stage of the polymerization by expressing the rate of depletion of monomer as

$$d[M]/dt = -k_{app}[M] \quad (\text{Eq. 10.6})$$

or

$$\ln[M] = -k_{app}t + \ln[M_0] + k_{app}t_0 = -k_{app}t + C \quad (\text{Eq. 10.7})$$

If the assumption of 1st order kinetics were indeed to hold, the model would then predict a linear variation for $\ln[M]$ with time t , and the apparent rate constant k_{app} would be given by the slope.

Figure 10.17 shows the individual MMA concentration vs. time plots for polymerizations at 7, 14, 21, 28, 35, and 42 MPa derived from the density information that were shown as a combined plot in Figure 10.14. The $\ln[M]$ vs t plot generated from this set of data is shown in Figure 10.18. Figure 10.19 shows the variation of $\ln[M]$ versus time for the initial 300 mins of polymerizations. It is easy to see that the rate constants increase with pressure. The rate constants evaluated from the slopes are shown in the figure and also in Table 10.3. The data show that rate constant increases from about 0.002 min^{-1} at 7 MPa to 0.008 min^{-1} at 42 MPa. A four-fold increase in rate constant is indicated.

Figure 10.20 shows the variations of [MMA] with time derived from the viscosity data for polymerizations at different pressures. Compared to Figure 10.17, these are more smooth variations. The Ln [M] vs time plots generated from these data are shown in Figure 10.21. Figure 10.22 shows the Ln [M] vs time plots for the first 400 min of polymerization time from which rate constants were again evaluated and are also included in Table 10.3. This set of data suggests a more modest and gradual increase in the rate constant from 0.004 min^{-1} at 7 MPa to 0.006 min^{-1} at 42 MPa. These are about 10 to 100-fold higher values compared to overall polymerization rate constants for MMA polymerizations at ambient pressure. As discussed in Chapter 2, high pressure polymerization generally increases the rate. This is because the activation volumes for most polymerizations are negative, and the pressure increase is related to the activation volume through:

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad (\text{Eq.10.8})$$

Using the estimated values of k from the viscosity measurement, we have estimated the activation volume. The ΔV^\ddagger has been calculated to be $-32.2 \text{ cm}^3/\text{mol}$. In the literature for bulk polymerization of MMA at $30 \text{ }^\circ\text{C}$, activation volume has been reported as $-17 \text{ cm}^3/\text{mol}$ (Jenner, 1978). A greater activation volume here may be attributed to the presence of solvent acetone and the higher polymerization temperature ($70 \text{ }^\circ\text{C}$).

Even though we did not carry out the evaluations, one can use the viscosity data to estimate k values for the second stage of polymerization which should be lower than the values in the first stage. Table 10.2 gives the $\frac{d\eta}{dt}$ for each stage at different pressures. The two-stage viscosity regions and polymerization rates are interesting features that have not been

discussed in the literature for MMA polymerizations. These are homogeneous polymerizations, as such the different rates should not be associated with phase separation, but rather, with the reduction in monomer concentration with time, and the reduction in the rate of decrease of the monomer in the viscous medium for further growth.

In traditional bulk polymerization, the rise in viscosity will hinder the termination reactions and reduce heat dissipation leading to higher polymerization rates known as “Trommsdorff” effect. The present data show that the system kinetics change, but the rate of viscosity increase in the second range is not greater than that in the first stage (Table 10.2). Polymerization appears to enter a second stage and not display “Trommsdorff” effect probably because the polymerizations are solution polymerizations, and not bulk polymerizations.

10.7 Summary and conclusions

For the first time systematic viscosity and density data have been generated for a polymerization system at high pressures in a dense fluid in real time. The measurements are very powerful in showing the shifts in the rate of polymerization. In polymerization of methyl methacrylate in acetone, the time for transition from the initial rate region to second stage where the rate of polymerization is decreased is observed to be pressure dependent. All polymerizations led to polydispersities around 1.5. A simple approximate kinetic analysis shows that apparent overall rate constant is increased with pressure, and they are approximately 10 to 100-fold greater than ambient pressure values.

Table 10.1 High-pressure homogeneous homopolymerization of methyl methacrylate in acetone at 343 K with 0.04 wt % AIBN as initiator

Reactant system						
MMA (10 wt %) + Acetone (90 wt %)						
Pressure (MPa)	7	14	21	28	35	42
Conversion (%)	82	82	79	90	85	91
M_w	23,500	23,900	24,300	46,600	42,100	42,200
M_n	15,100	15,100	15,900	32,360	29,000	28,900
PDI	1.56	1.58	1.53	1.44	1.45	1.46

Table 10.2 Changing rates of densities and viscosities in both the early and late stages of the polymerizations and the transition time between the two stages at different pressures

P/MPa	Rate of change in density (g/(cm ³ min))		Transition time for rate of change in density (min)	Rate of change in viscosity (mPa·s/min)		Transition time for rate of change in viscosity (min)
	Early stage × 10 ⁵	Late stage × 10 ⁶		Early stage × 10 ⁴	Late stage × 10 ⁴	
7	2.2	8.2	360	4.9	3.3	420
14	2.6	8.2	260	5.8	4.5	360
21	2.2	11.7	240	7.9	5.8	320
28	3.4	8.9	260	10.8	7.6	320
35	2.6	15.3	260	12.3	7.5	320
42	3.8	15.6	260	13.2	7.5	320

Table 10.3 Apparent overall rate constants for MMA polymerizations in acetone at different pressures s estimated from change in density or viscosity

P / MPa	$k_{app} / \text{min}^{-1}$ (from density)* $\times 10^4$	$k_{app} / \text{min}^{-1}$ (from viscosity)** $\times 10^4$
7	16.6	37.8
14	52.0	45.4
21	58.4	51.8
28	62.7	58.8
35	41.9	58.3
42	82.3	58.2

* The time range for evaluation is first 300 mins of the polymerizations;

** The time range for evaluation is first 400 mins of the polymerizations.

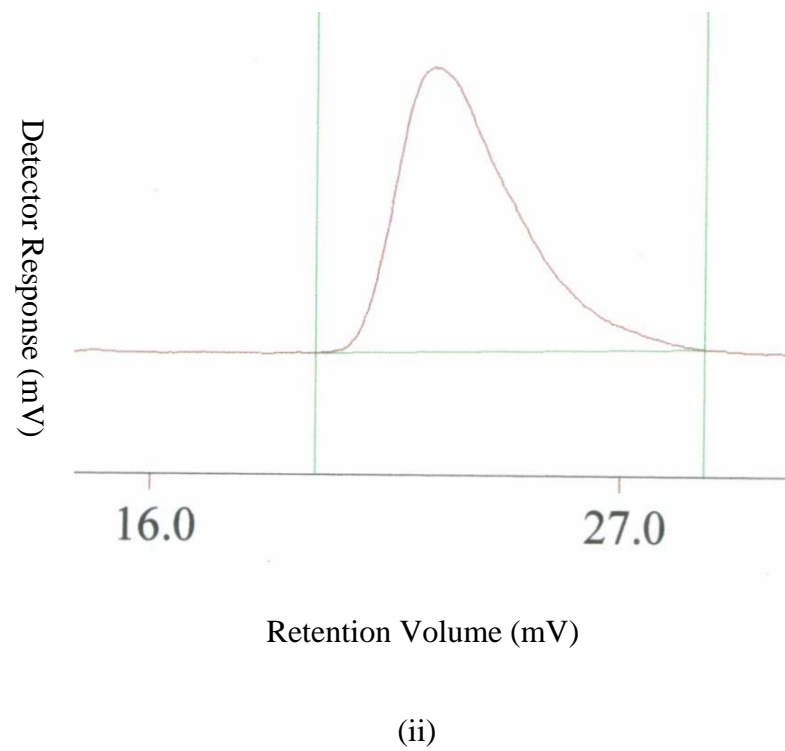
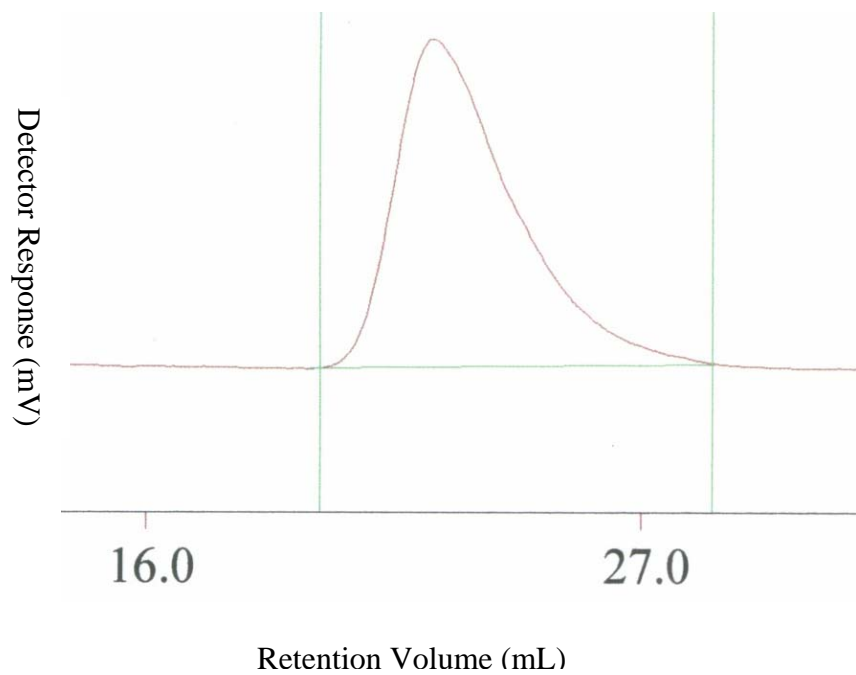


Figure 10.1 GPC tests for PMMA samples formed from the MMA polymerizations in acetone at (i) $P = 28$ MPa; (ii). $P = 35$ MPa.

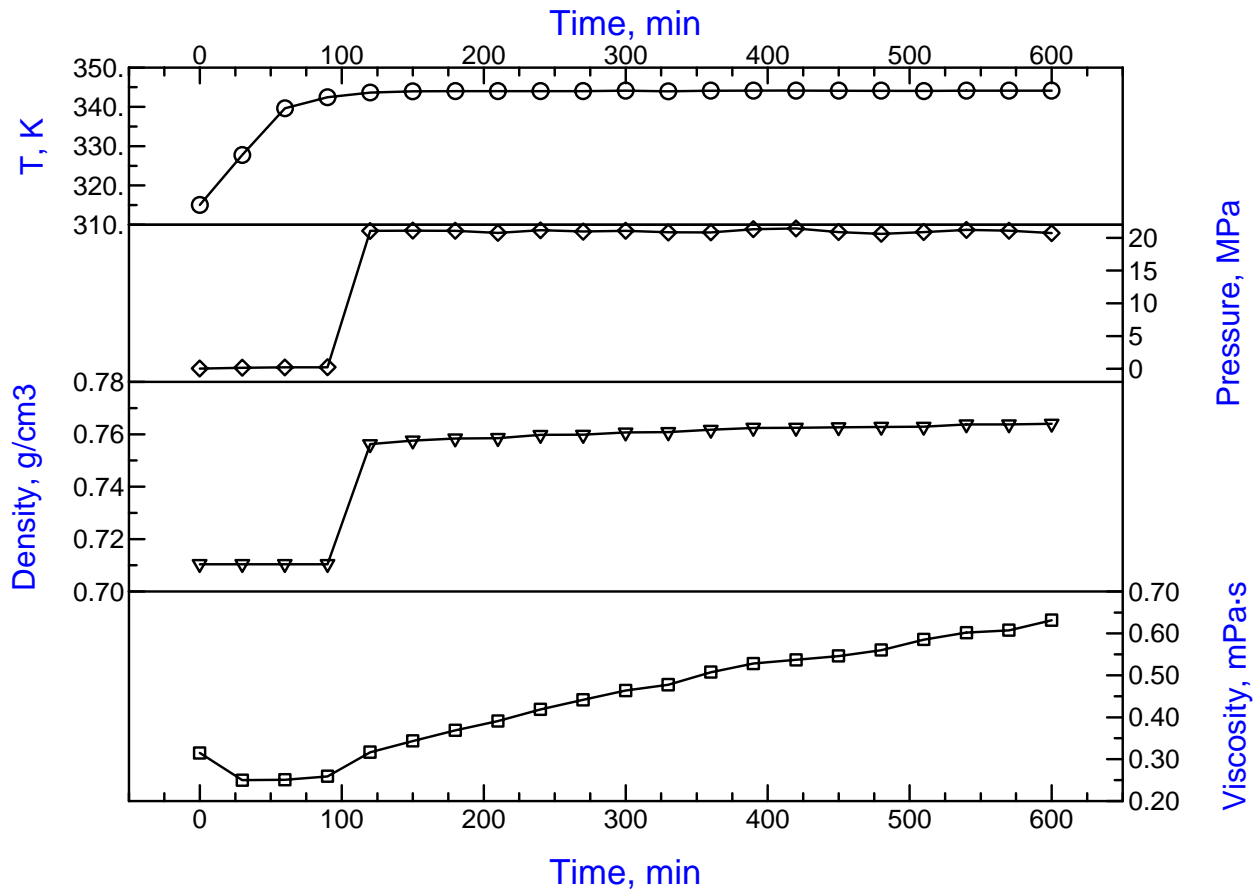


Figure 10.2 Variation of temperature, pressure, density, and viscosity with time during polymerization at 21 MPa (Initial reactant mixture is MMA (10 wt %) + Acetone (90 wt %) + AIBN (0.04 wt %)).

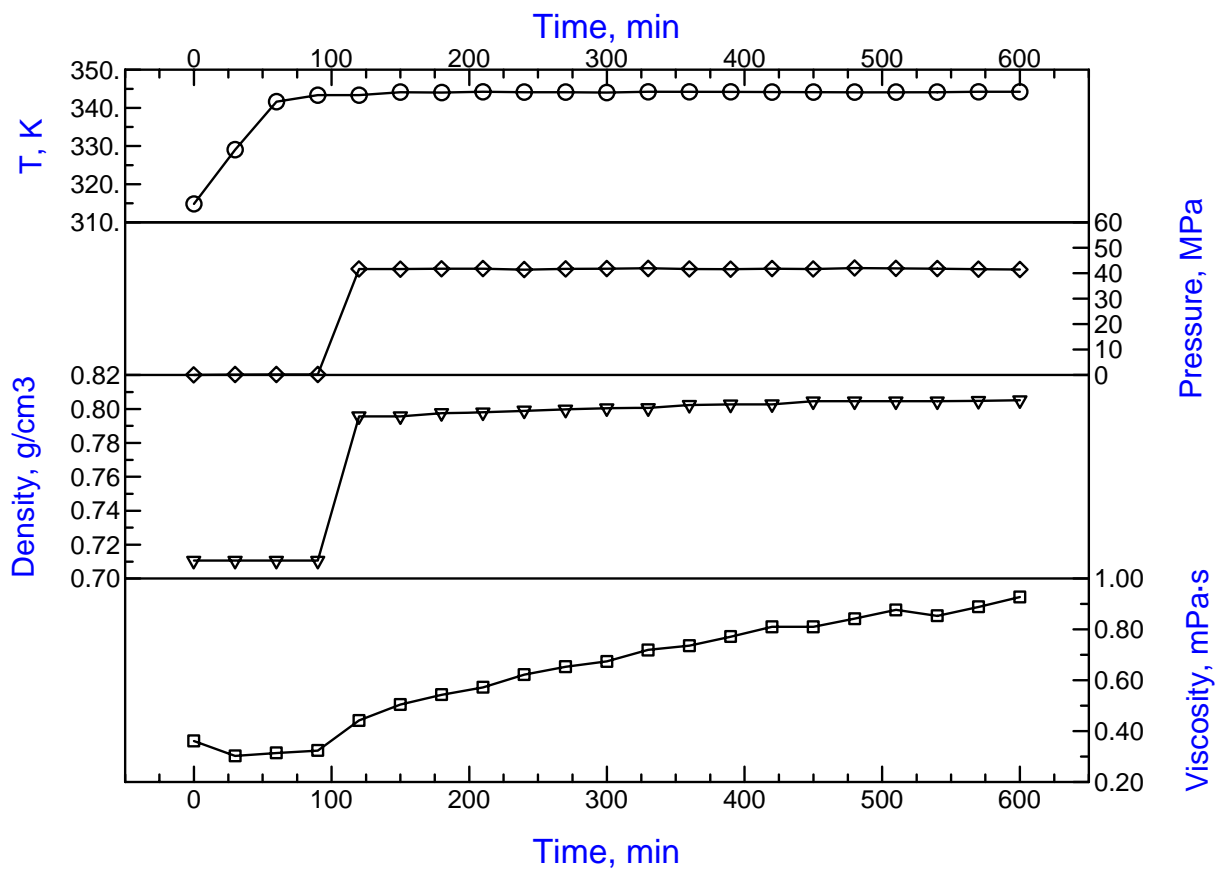


Figure 10.3 Variation of temperature, pressure, density, and viscosity with time during polymerization at 42 MPa (Initial reactant mixture is MMA (10 wt %) + Acetone (90 wt %) + AIBN (0.04 wt %)).

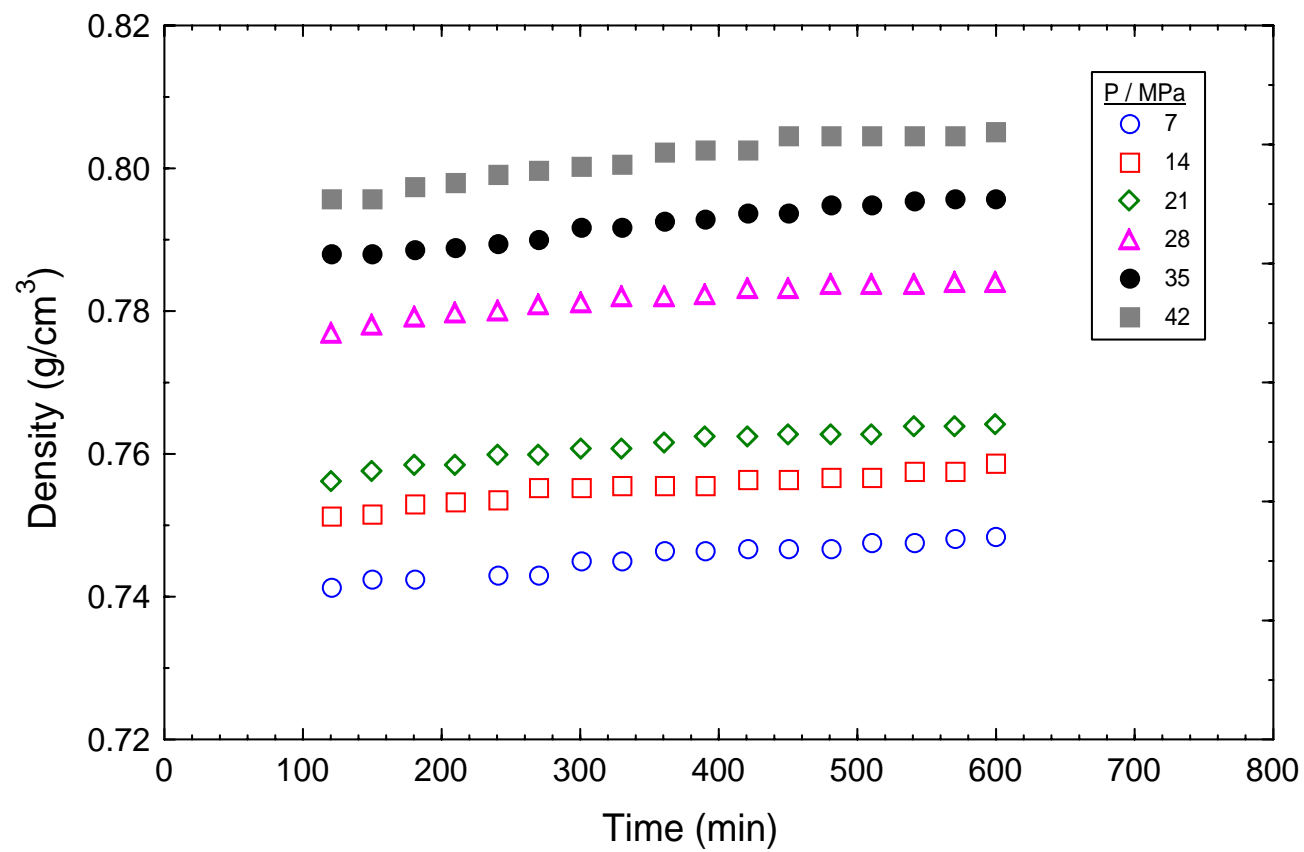


Figure 10.4 Variation of density with time during polymerizations at different pressures (Initial reactant mixture is MMA (10 wt %) + Acetone (90 wt %) + AIBN (0.04 wt %)).

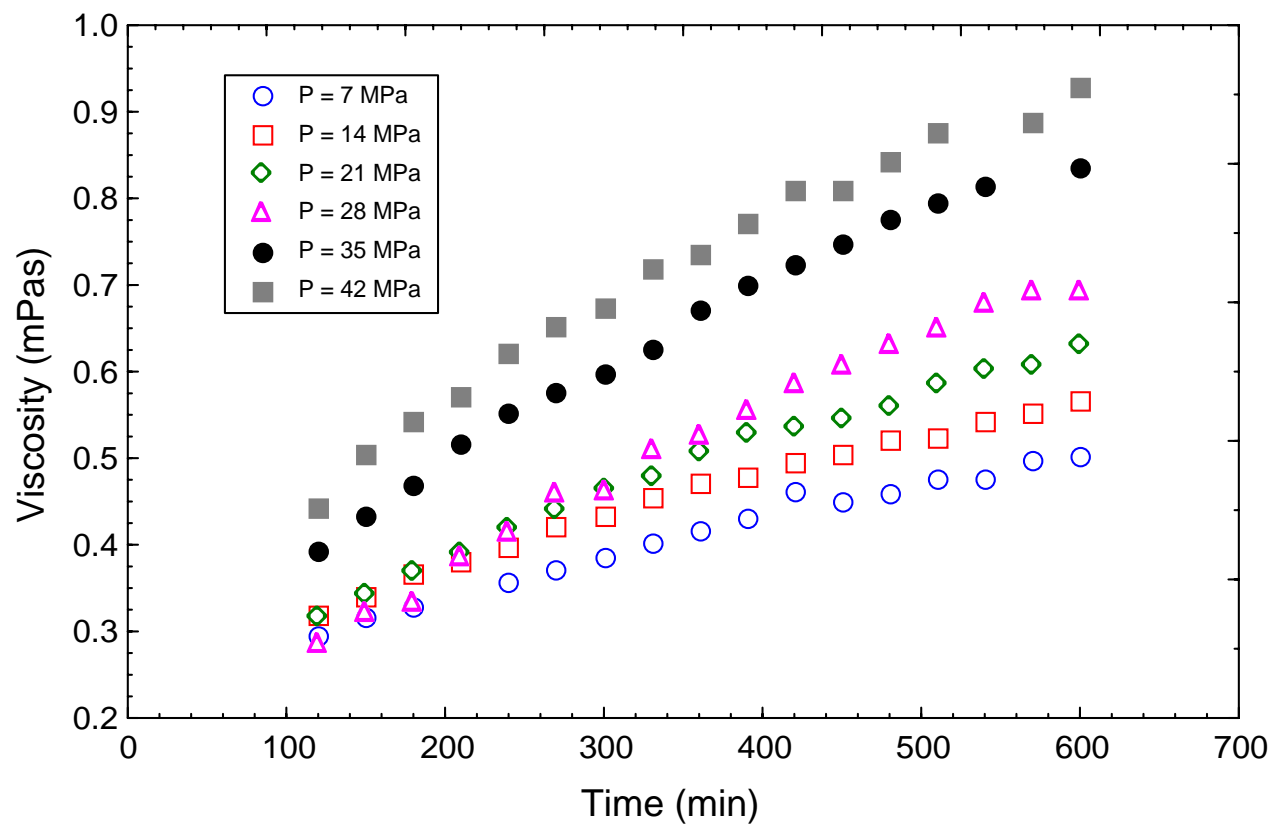


Figure 10.5 Variation of viscosity with time during polymerizations at different pressures.

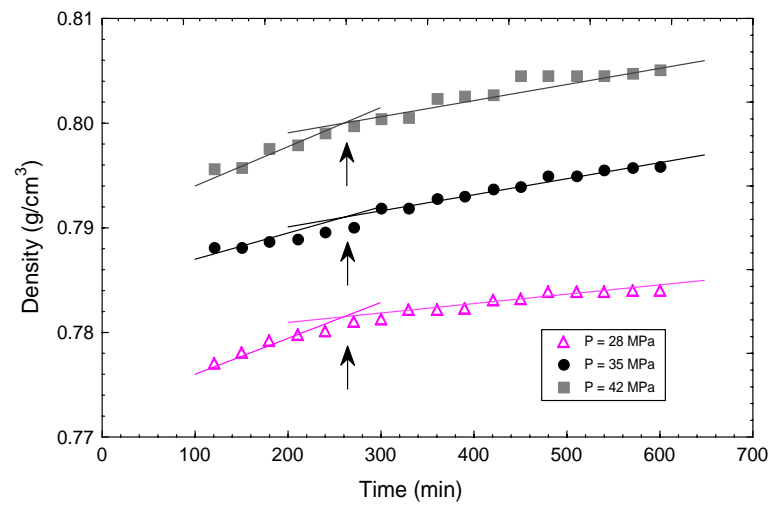
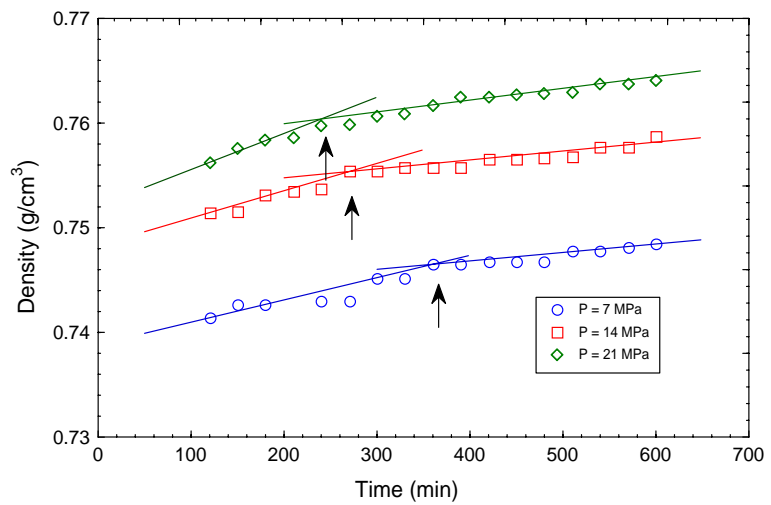


Figure 10.6 Variation of density with time during polymerization at different pressures.

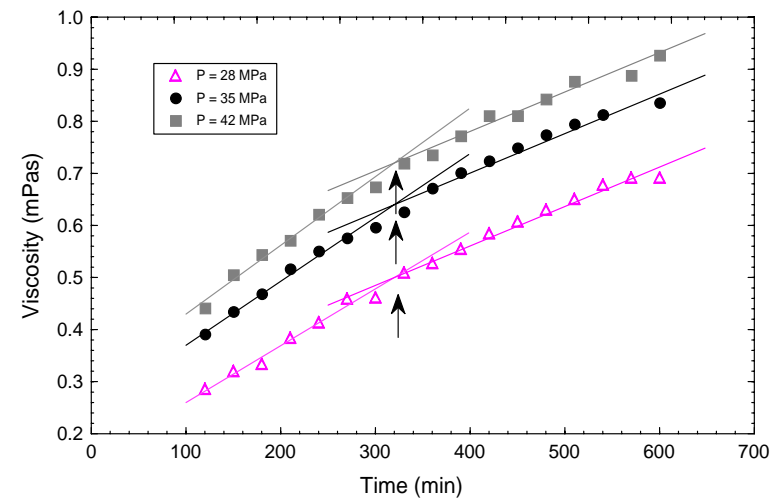
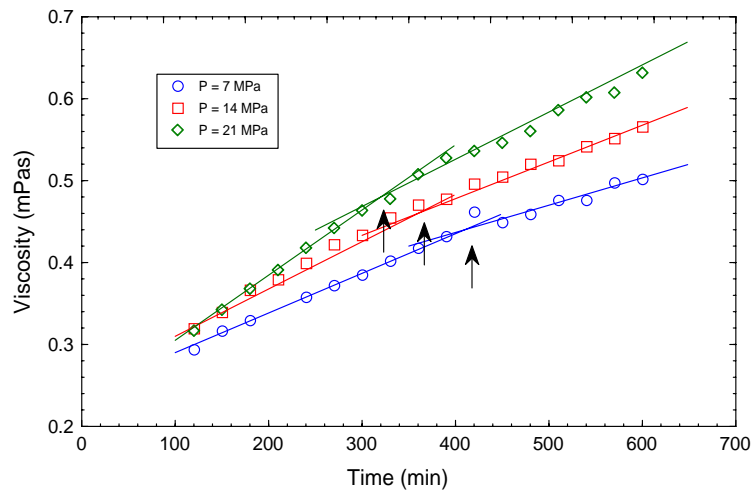


Figure 10.7 Variation of viscosity with time during polymerization at different pressures.

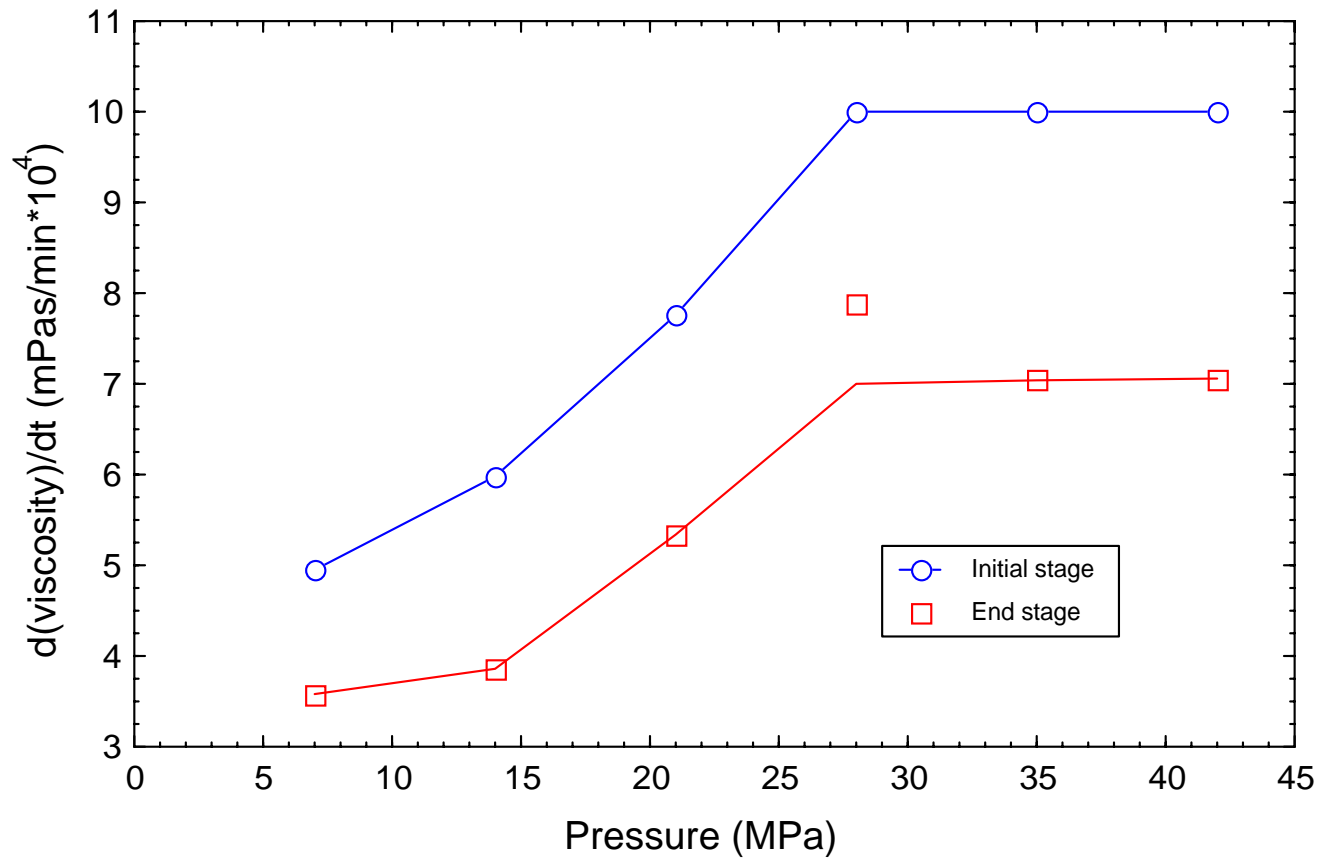


Figure 10.8 Variation of viscosity changing rate with pressure for two stages.

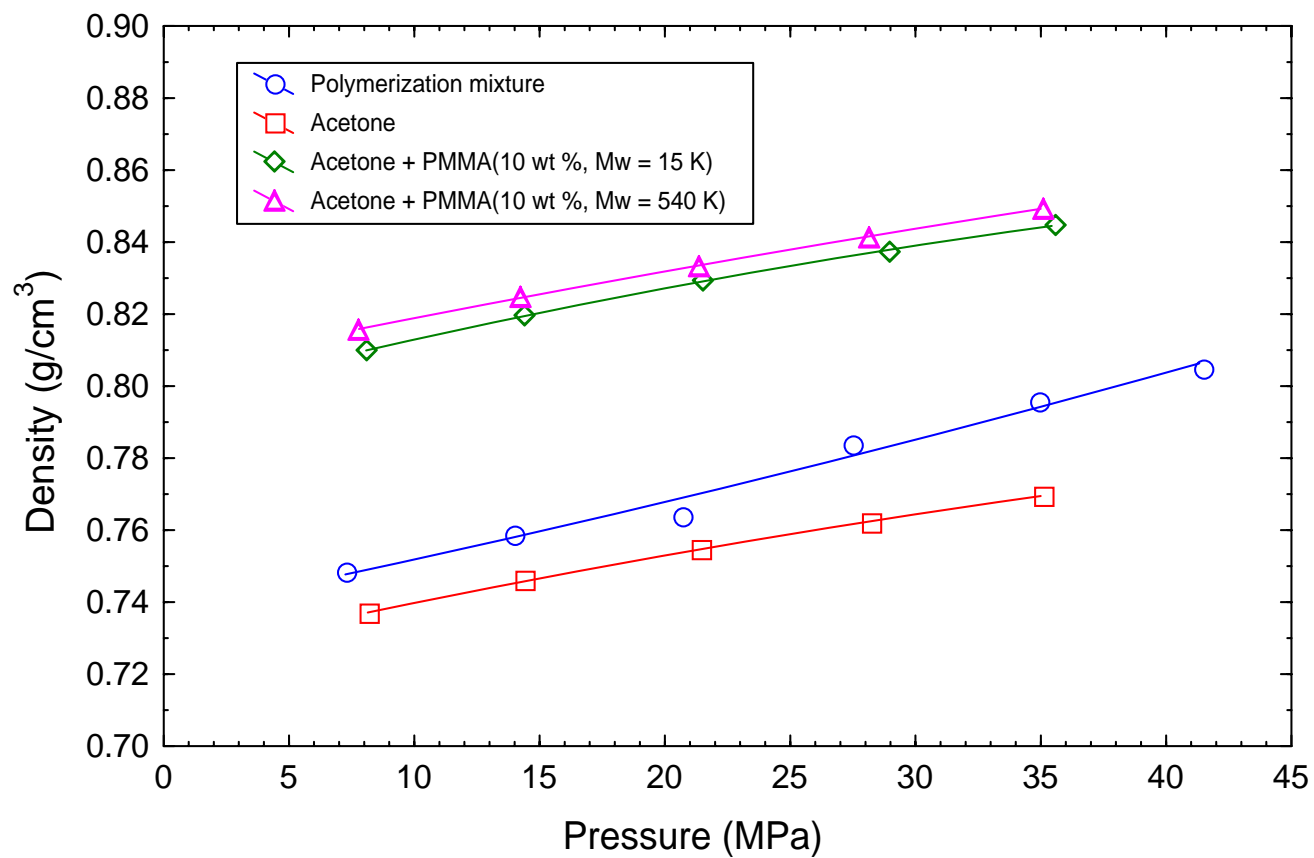


Figure 10.9 Density comparisons between present reactant mixtures and other three systems (acetone, 10 wt % PMMA ($M_w = 15$ K) solution in acetone, 10 wt % PMMA ($M_w = 540$ K) solution in acetone).

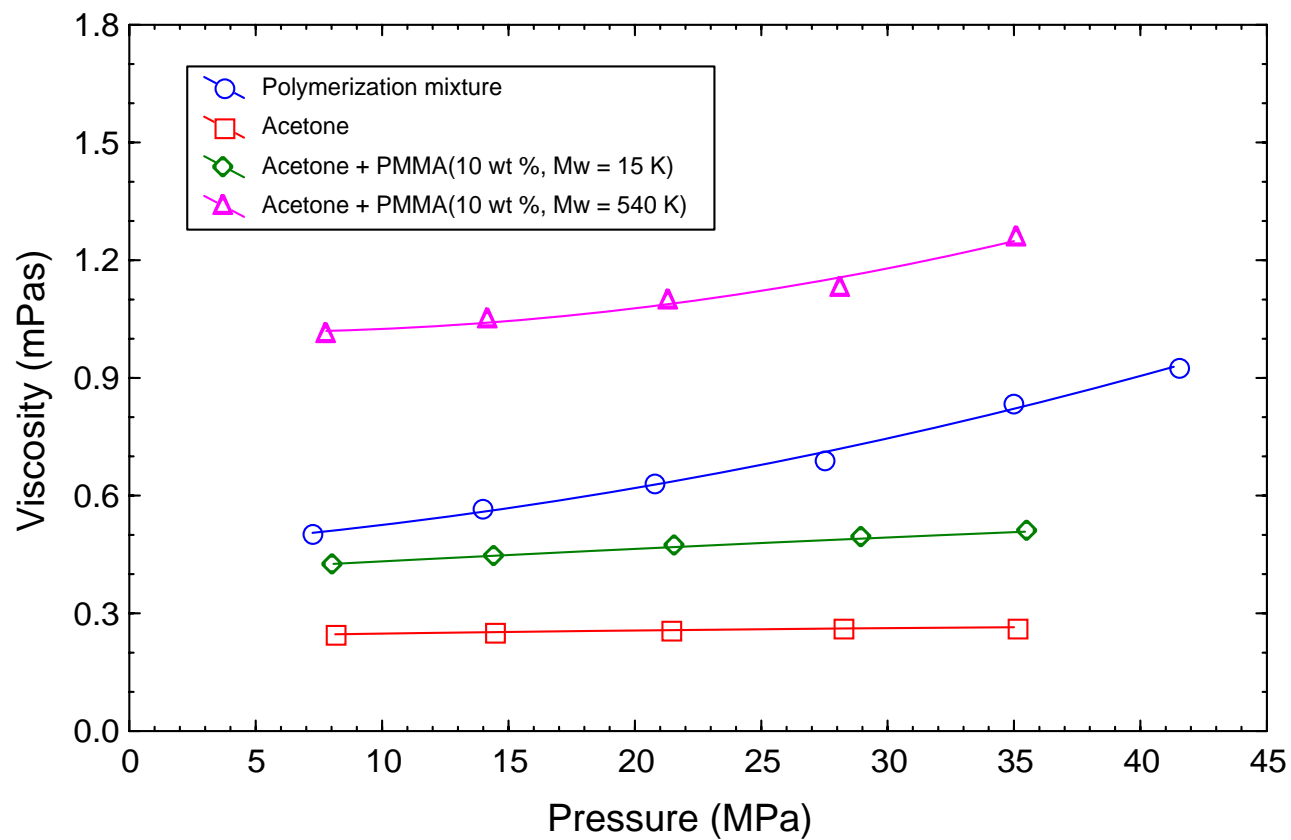


Figure 10.10 Viscosity comparisons between present reactant mixtures and other three systems (acetone, 10 wt % PMMA ($M_w = 15$ K) solution in acetone, 10 wt % PMMA ($M_w = 540$ K) solution in acetone).

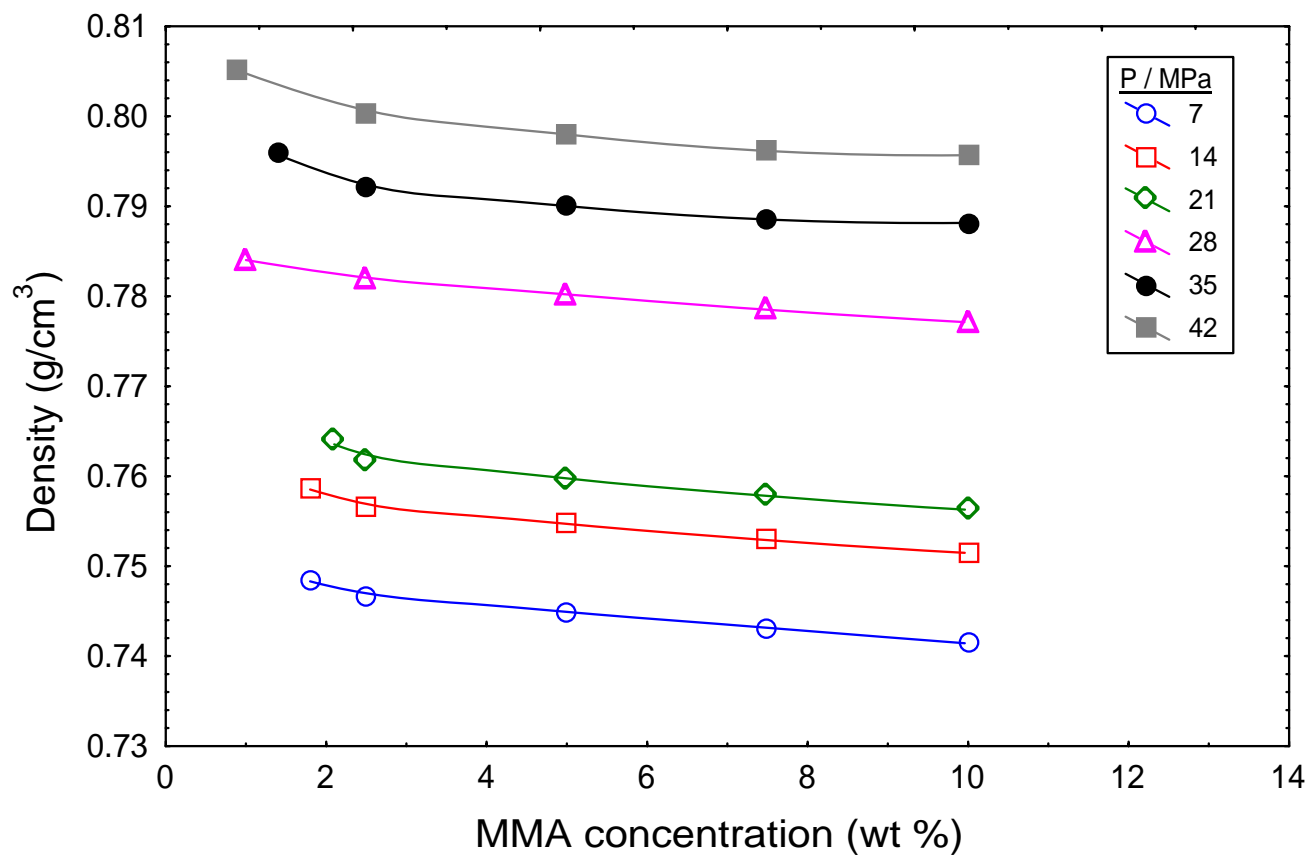


Figure 10.11 Variation of density with MMA concentration for PMMA + MMA + acetone mixture at 7, 14, 21, 28, 35, and 42 MPa. The concentration of PMMA + MMA is fixed at 10 wt %.

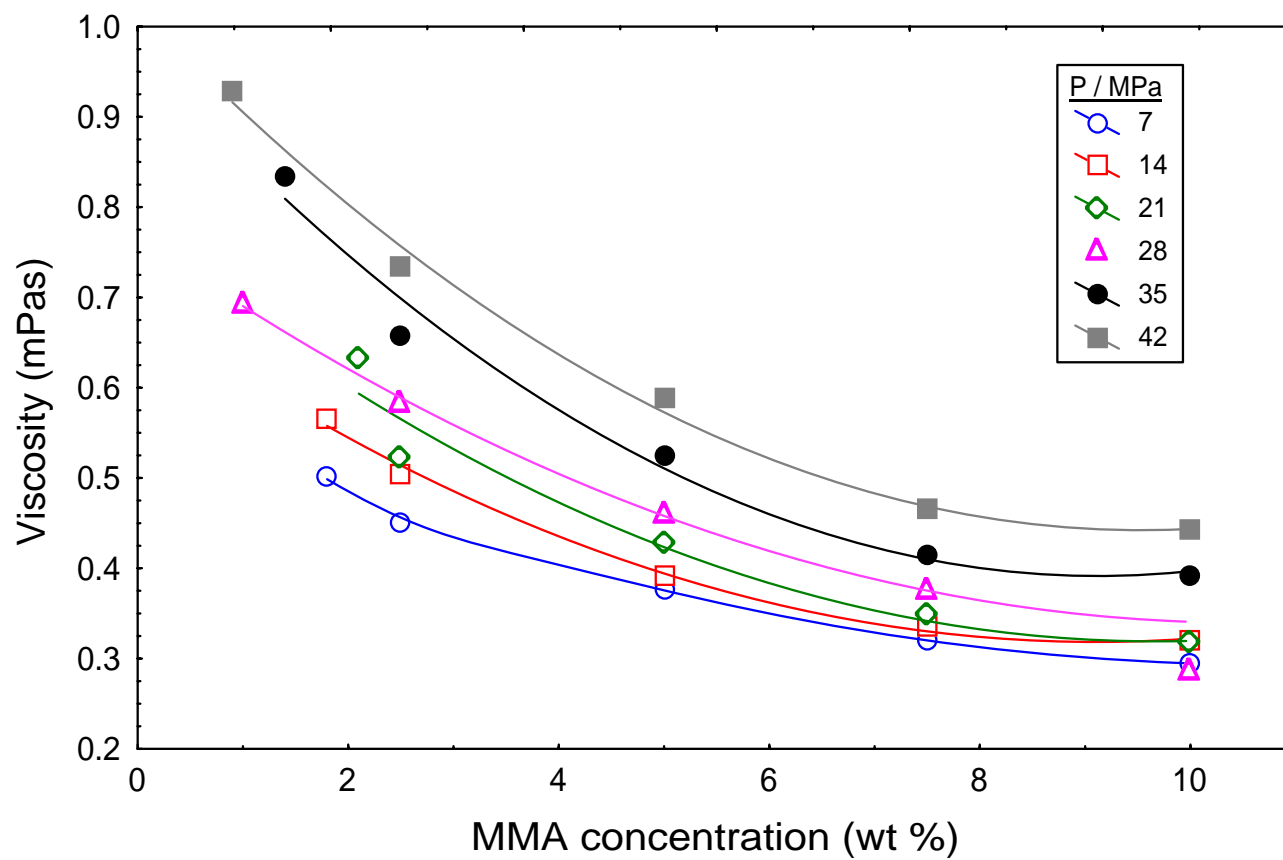


Figure 10.12 Variation of viscosity with MMA concentration for PMMA + MMA + acetone mixture at 7, 14, 21, 28, 35, and 42 MPa. The concentration of PMMA + MMA is fixed at 10 wt %.

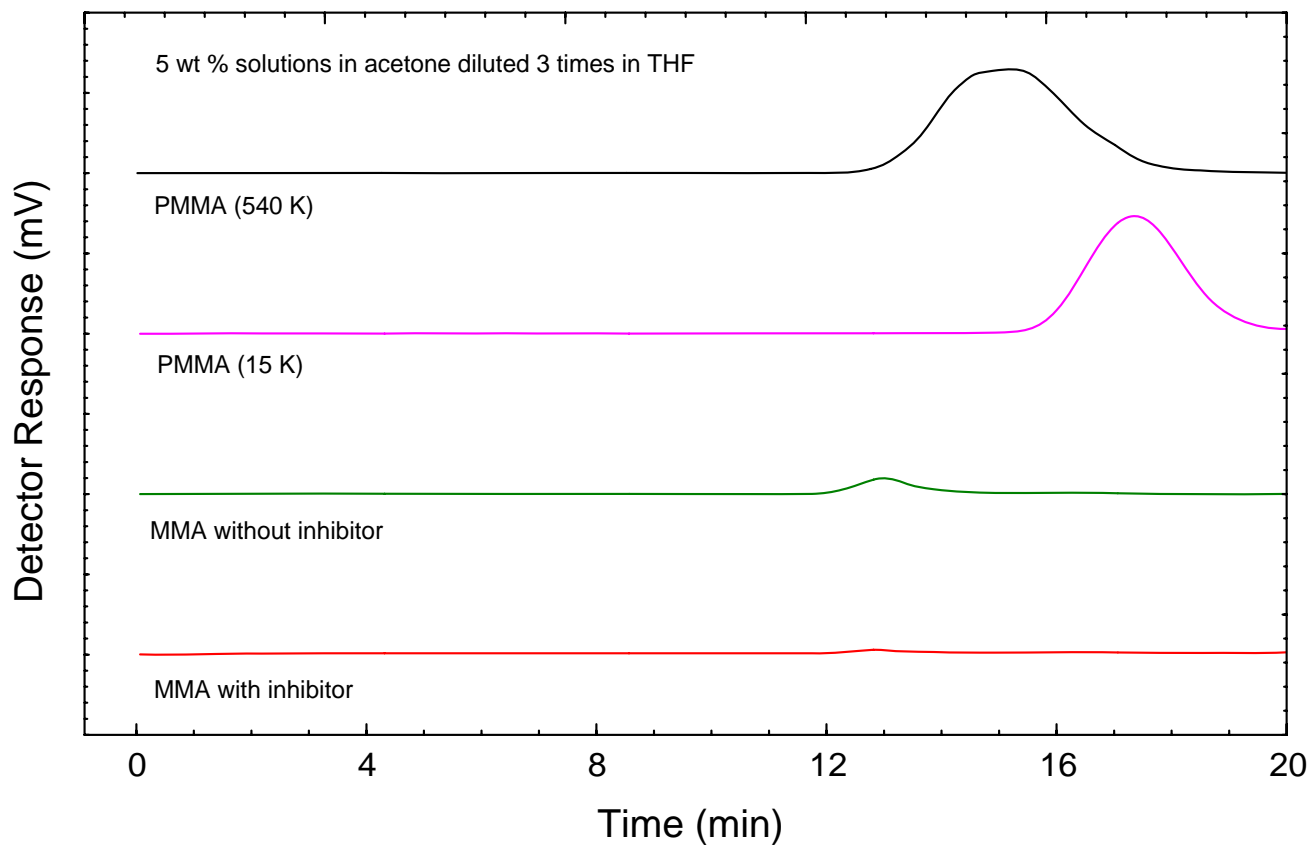


Figure 10.13 Comparison of the GPC elution times for 5 wt % PMMA solutions ($M_w = 15$ K and $M_w = 540$ K) with the elution times for 5 wt % MMA solutions in acetone that were kept in the viscometer at 343 K for 24 hours. For the GPC runs, the solutions were diluted 3 times with THF.

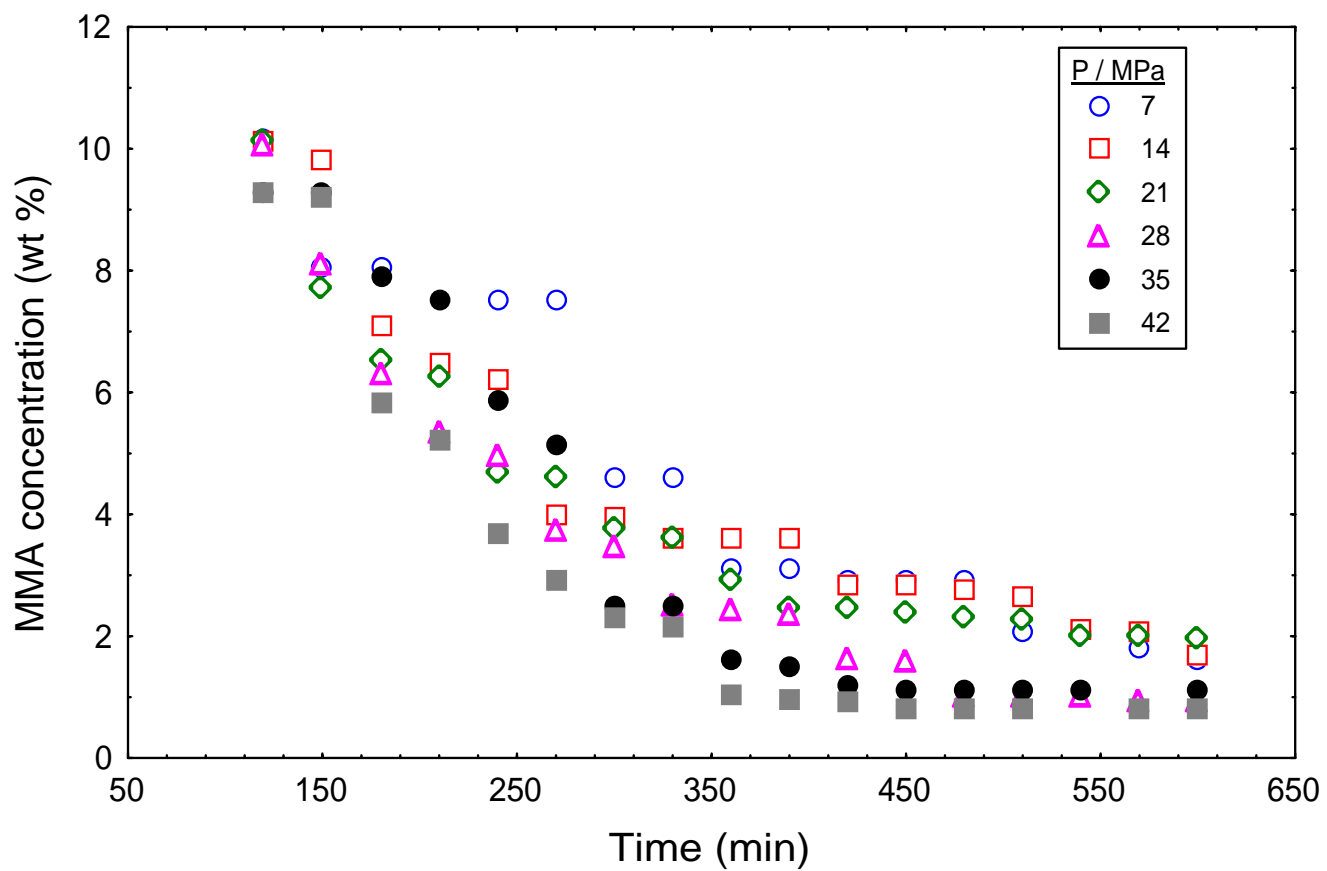


Figure 10.14 Variation of MMA concentration with time derived from density data at different pressures.

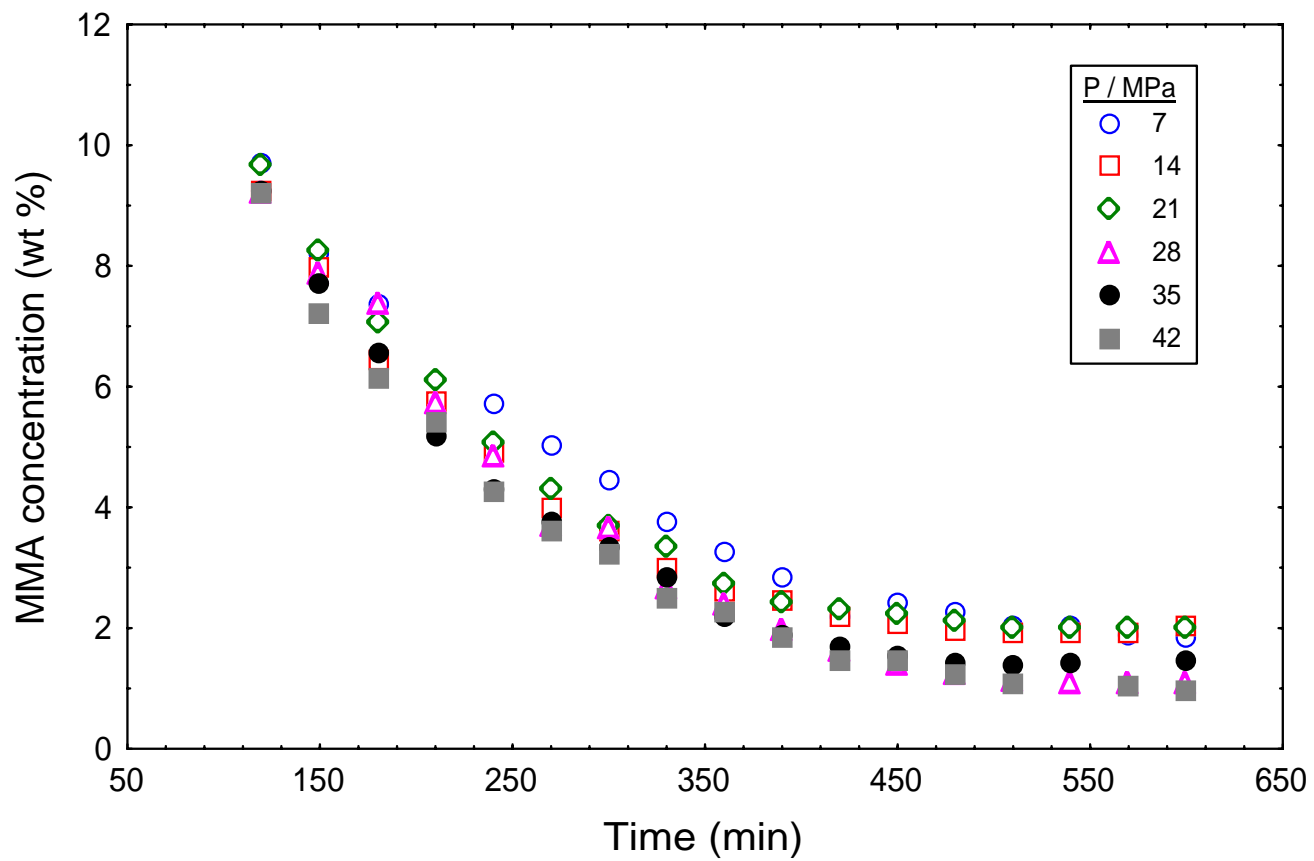


Figure 10.15 Variation of MMA concentration with time derived from viscosity data at different pressures.

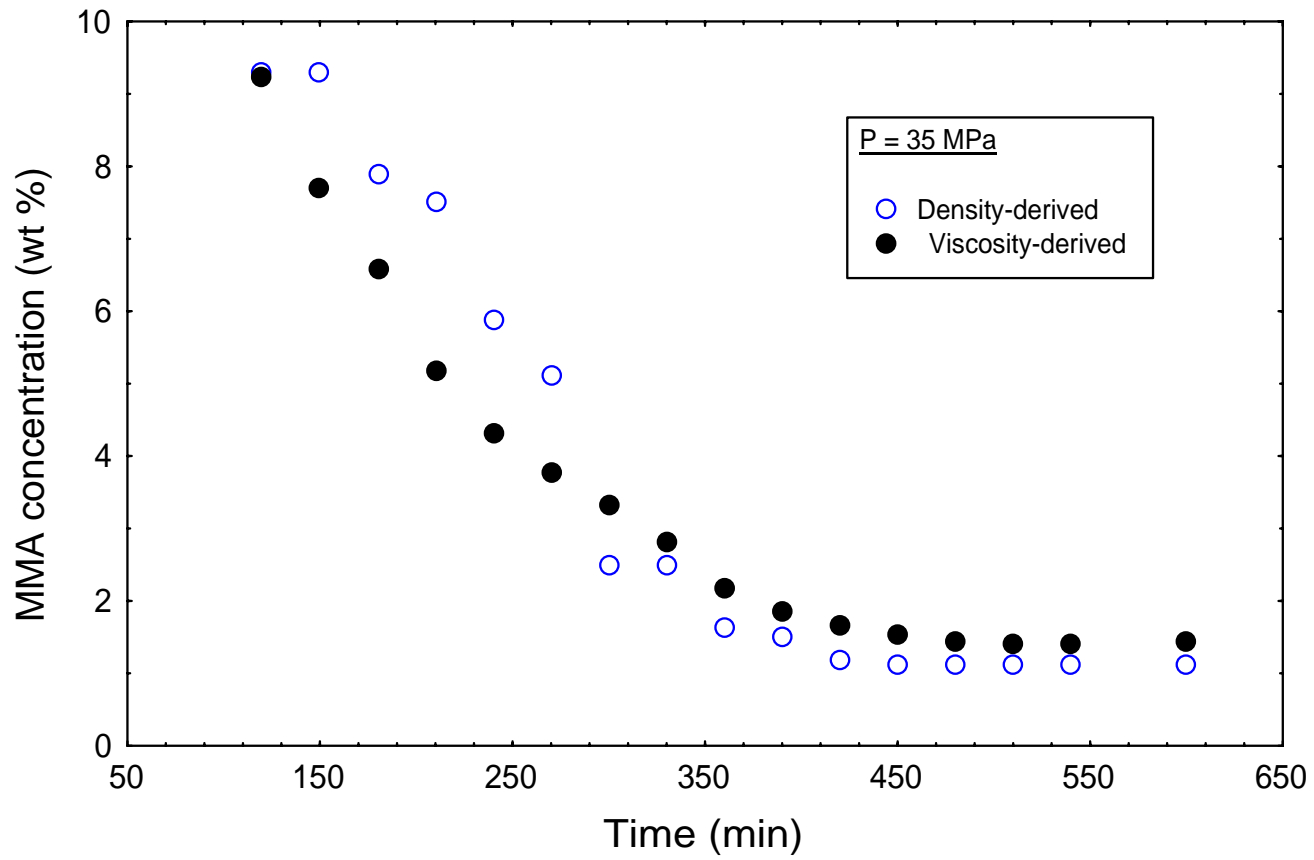


Figure 10.16 Comparison of density-derived and viscosity-derived variation of MMA concentration with time at 35 MPa.

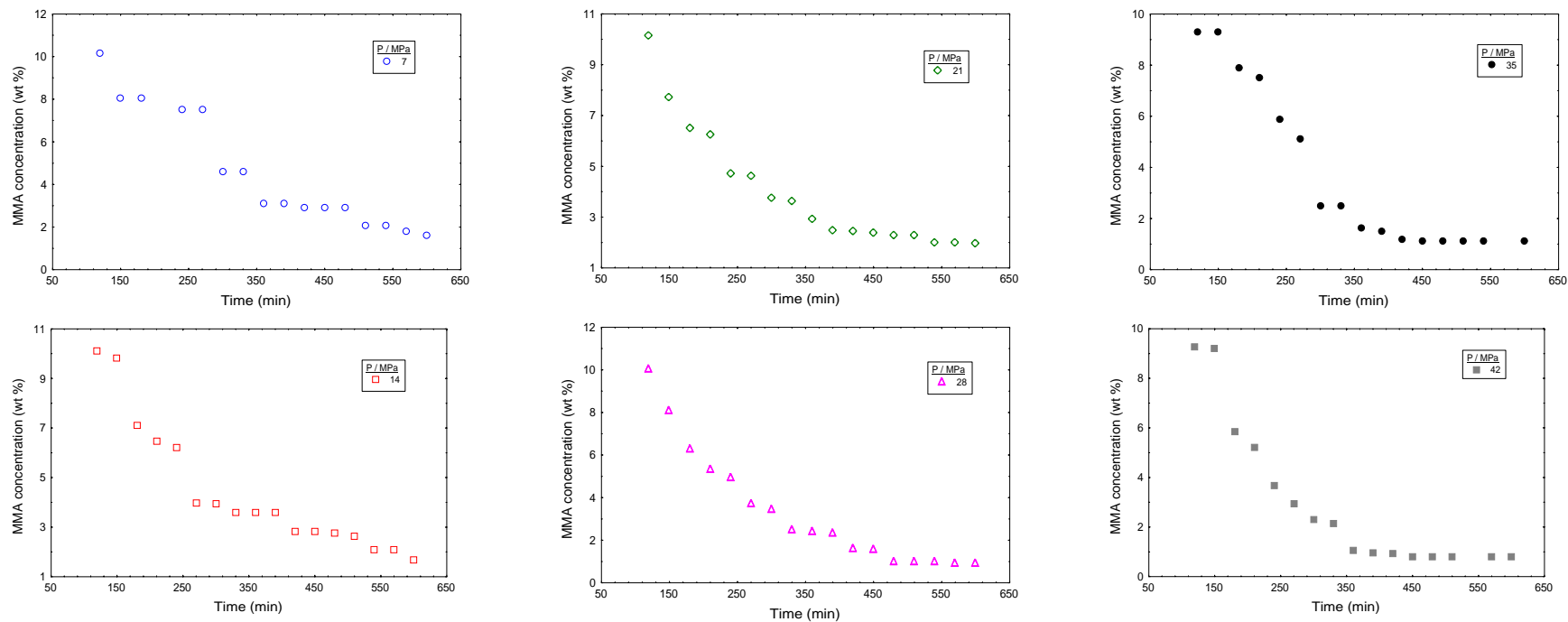


Figure 10.17 Variations of MMA concentration with time for polymerizations at different pressures. The MMA concentrations are derived from density information of the reaction mixtures. (See also Figure 10.14)

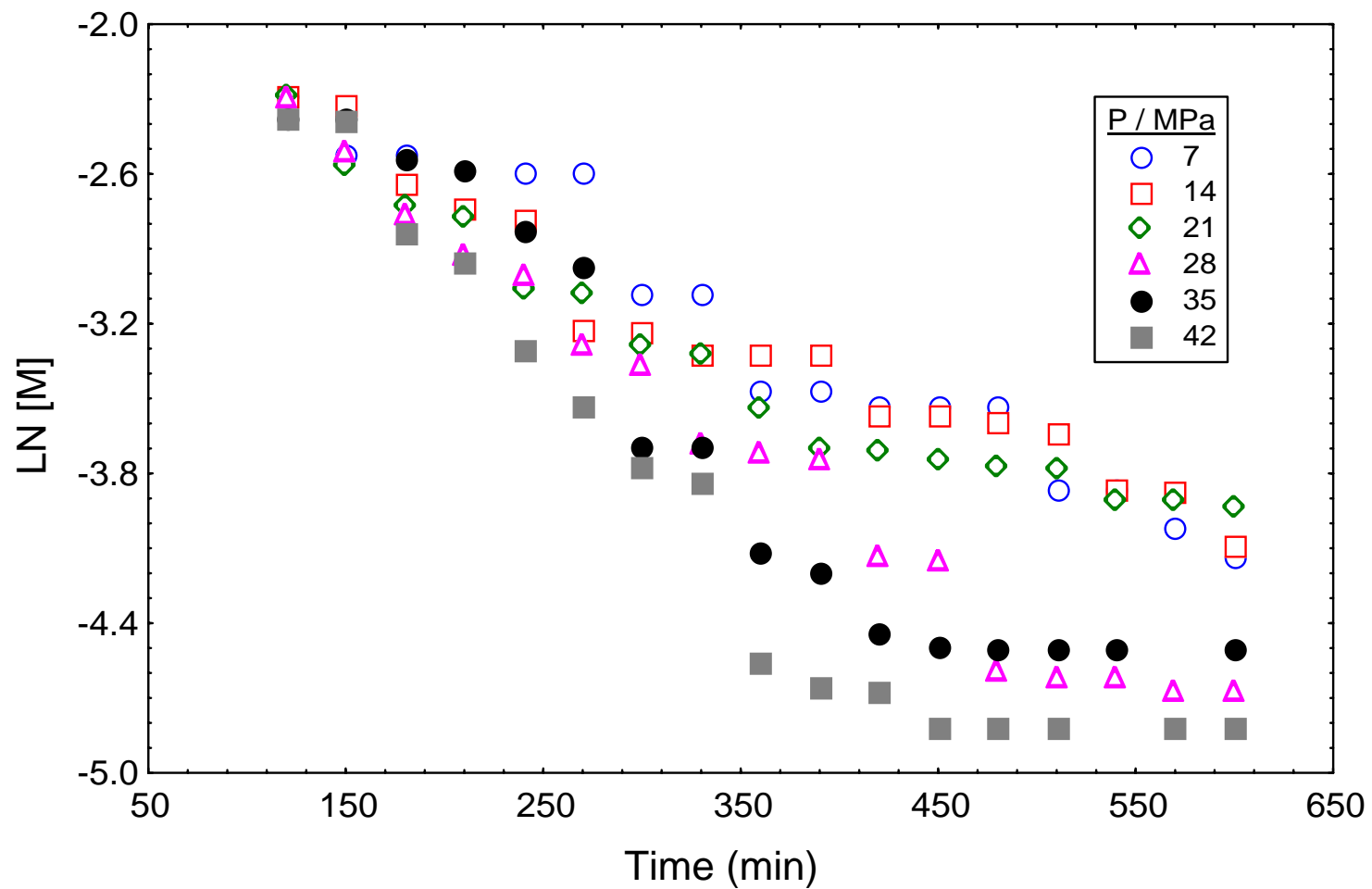


Figure 10.18 Variations of Ln [M] with time for polymerizations at different pressures.

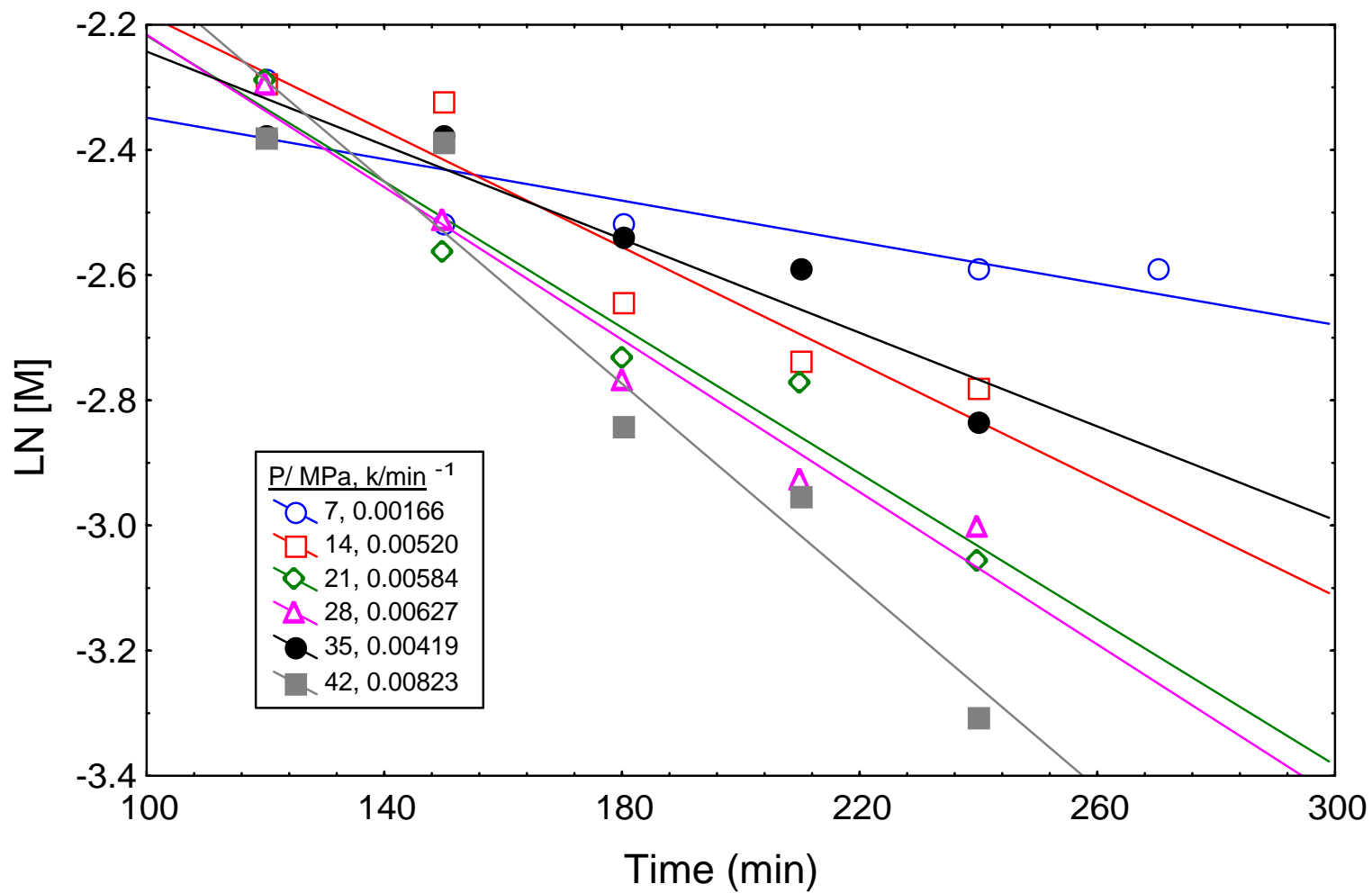


Figure 10.19 Ln [M] versus time plots for polymerizations in the initial 300 mins at different pressures from monomer concentrations estimated from the mixture density data for the evaluation of the apparent rate constant.

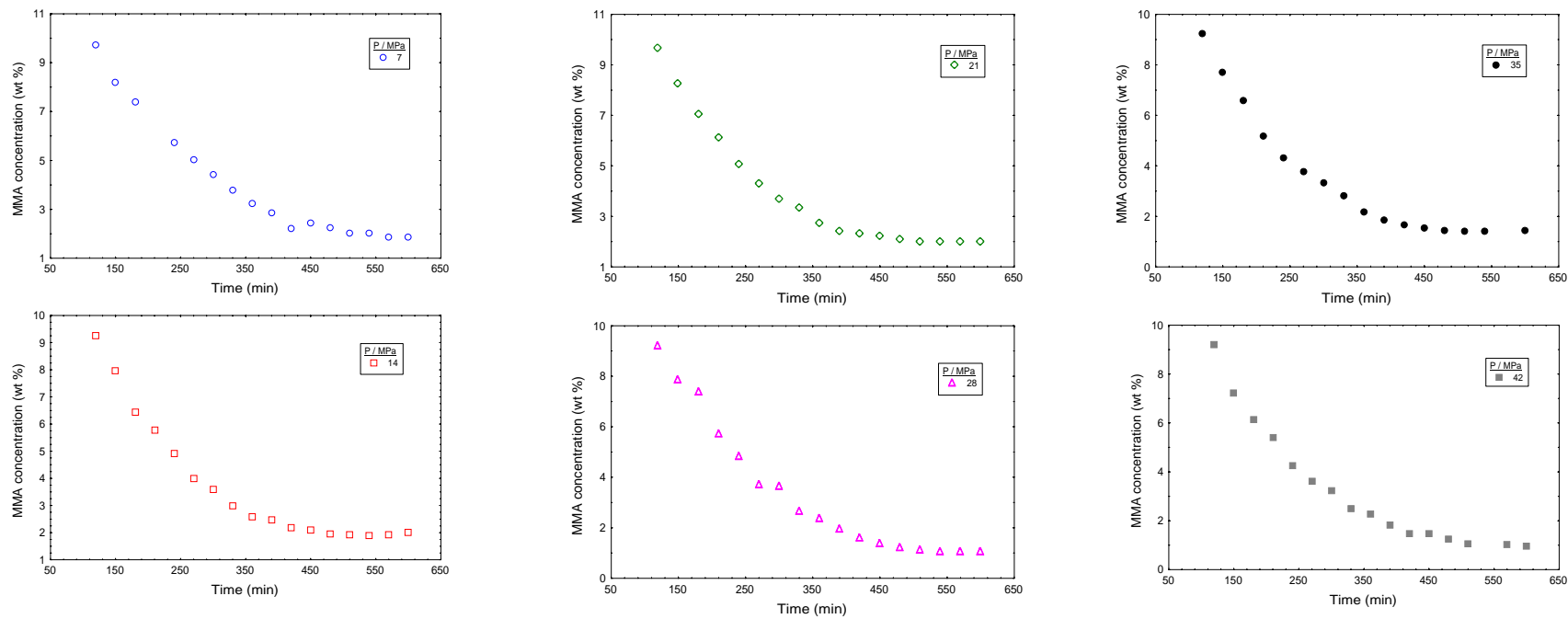


Figure 10.20 Variations of MMA concentration with time for polymerizations at different pressures. The MMA concentrations are derived from viscosity information of the reaction mixtures.

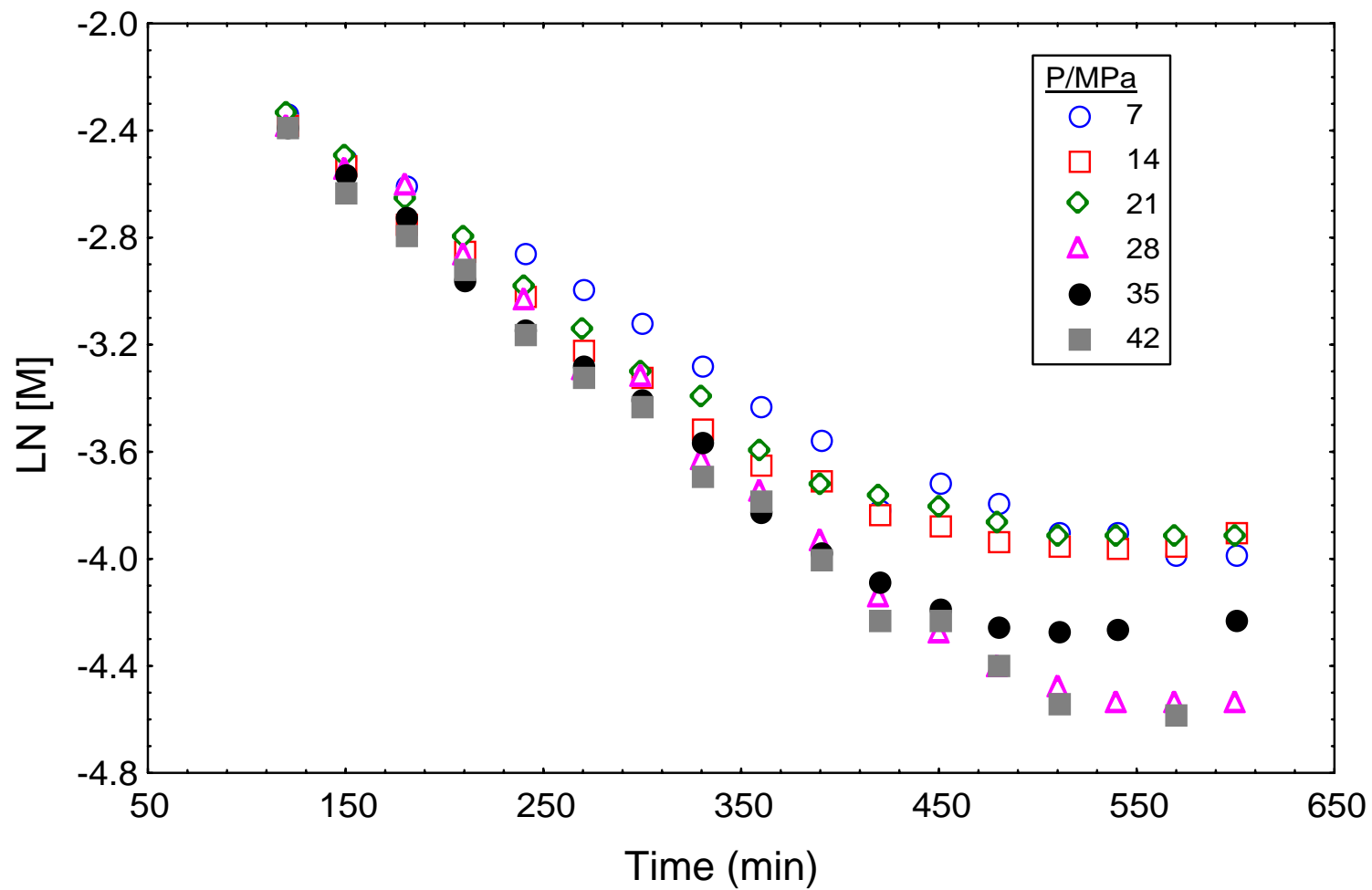


Figure 10.21 Variations of Ln [M] with time for polymerizations at different pressures.

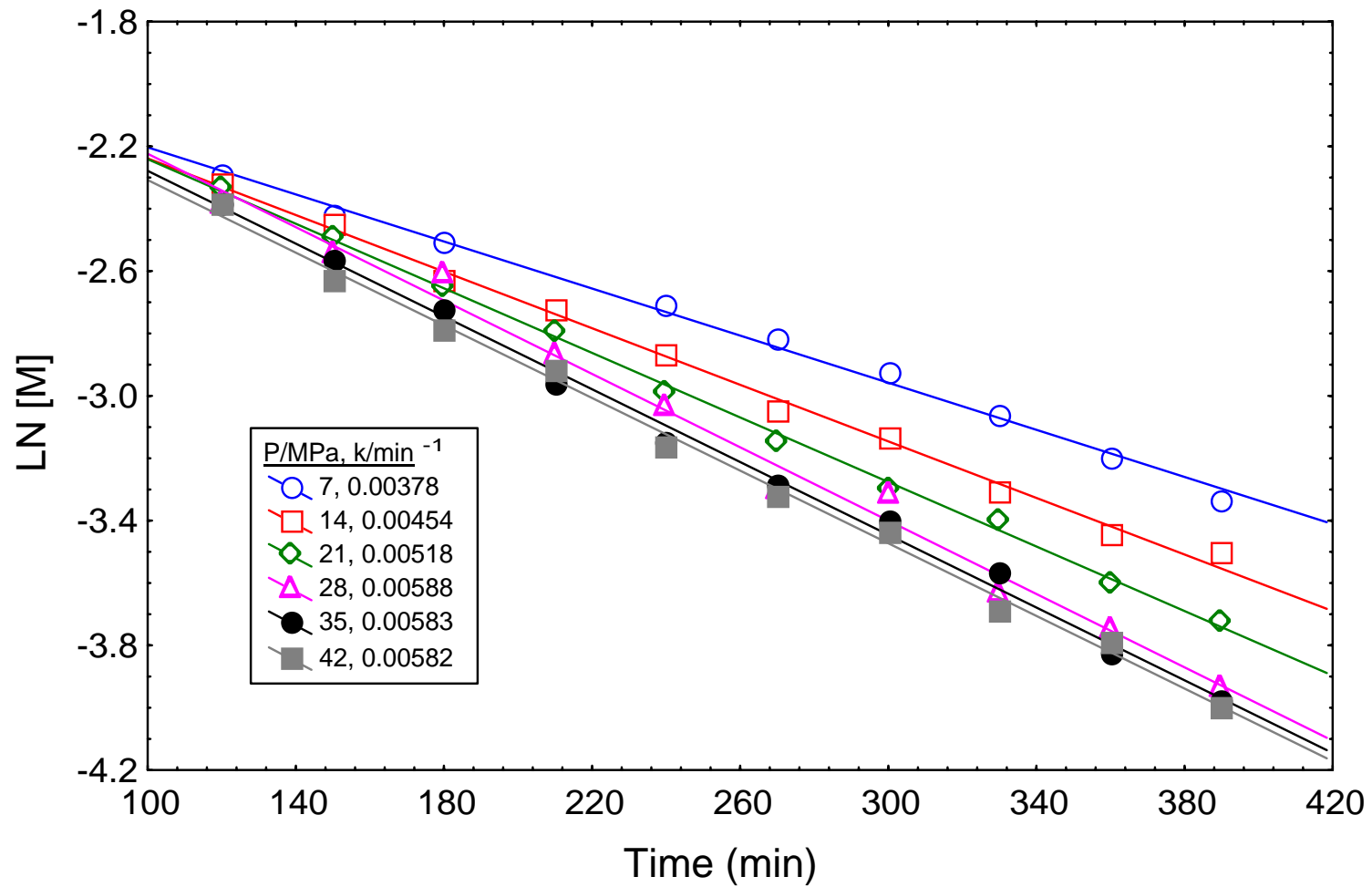


Figure 10.22 Ln [M] versus time plots for polymerizations in the initial 300 mins at different pressures from monomer concentrations estimated from the mixture viscosity data for the evaluation of the apparent rate constant.