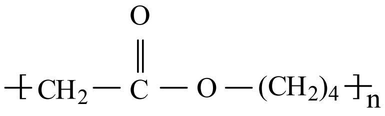
CHAPTER 11

HOMOPOLYMERIZATION AND COPOLYMERIZATIONS OF 2-METHYLENE-1,3-DIOXEPANE (MDO) IN CARBON DIOXIDE AT HIGH PRESSURES

Due to its wide application potential in biomedical devices (Xie et. al., 2006; Wu et. al., 1996; Reignier and Huneault, 2006) and in the formation of polymer blends (De Juana and Cortazar, 1993; Men and Strobl, 2003), alternative pathways for synthesis of poly (ε-caprolactone) are of practical importance (Jin and Gonsalves, 1997; 1998). The chemical structure of polycaprolactone is given in Figure 11.1.



$$\left[CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2)_4 \right]_n$$

Figure 11.1 Molecular structure for poly (ε-caprolactone).

There are several polymerization routes to produce PCL that involve different mechanisms and monomers. The common method is the ring-opening polymerization of ε-caprolactone using homogeneous organic metal complex catalysts such as tin (IV) alkoxide (Lecomte and Jerome, 2004), zinc alkoxide (Barakat et. al., 1991), or aluminum triflate (Wang and Kunioka, 2005). This is illustrated in Figure 11.2. This route is known to lead to a semicrystalline polymer without chain branching. However, the recovery and removal of catalysts is a problem in homogeneous polymerizations. The selection of catalyst is important in the eventual use of the polymer in biomedical applications where the catalyst removal is important. Indeed the use of Zn alkoxide has replaced tin (IV) alkoxide for biomedical constraints.

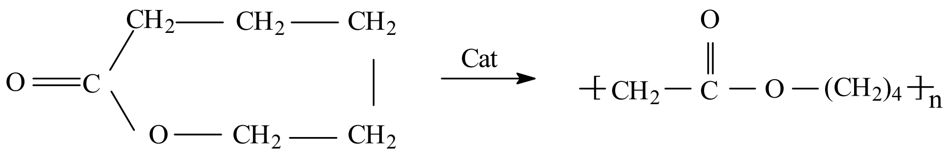


Figure 11.2 Catalyzed ring-opening polymerization of ε-caprolactone to produce poly (ε-caprolactone).

Free radical ring-opening polymerizations of 2-methylene-1,3-dioxepane (MDO), a cyclic ketene acetal, is another route to produce PCL (shown in Figure 11.3), which has been extensively studied at ambient pressure (Wei et. al., 1996; Jin and Gonsalves, 1997, 1998; Sun et. al., 2003a, b; Hiraguri et. al., 2004). It is reported that MDO undergoes a 100 % ring opening polymerizations (Jin and Gonsalves, 1997). This ring-opening polymerization is also reported to lead to low volume shrinkage making the polymer attractive as dental material (Wei et. al., 1996). Unlike the ring opening polymerization of ε-caprolactone, the polymerization of MDO proceeds by a backbiting mechanism which leads to branching. In this context, PCL produced by MDO polymerization are different than PCL produced by polymerization of ε-caprolactone even though they are both ring opening polymerizations. The most significant consequence is the lack of crystallinity in PCL that forms from MDO. This is because branching prevents crystallization. The reaction mechanism leading to branching in MDO polymerization is illustrated in the Figure 11.4 (Jin and Gonsalves, 1997). The 1,7- and 1,4-H transfers are the cause for branching. They have been confirmed by ^{1}H and ^{13}C NMR characterizations of the polymers produced at ambient pressure (Jin and Gonsalves, 1997).

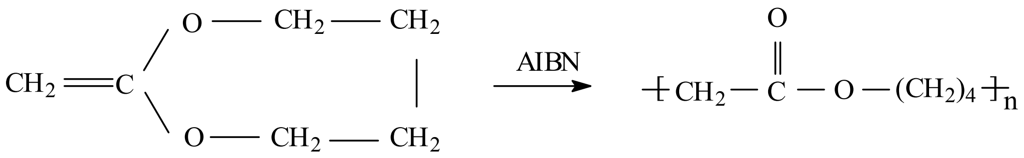


Figure 11.3 Ring opening polymerization of 2-methylene-1,3-dioxepane (MDO) to produce poly (ε-caprolactone).

Even though the free radical polymerization of MDO provides a catalyst-free route to produce PCL, it has been difficult to produce high molecular weight polymers. The end products are waxy solids or even viscous liquids arising from either the low molecular weights or from the branching that lower T_g. The copolymerizations of MDO have been a route to produce polymers with higher molecular weights or higher T_g's. Copolymerizations have been used to incorporate pendant functional groups into the polymer chain. Copolymerizations have been used to alter the degradability of PCL and also to prepare polymer-drug or polymer-biomolecule conjugates for drug delivery applications. Copolymerizations of MDO with methyl acrylate, vinyl phosphonic acid (Jin and Gonsalves, 1998), dimethyl vinylphosphonate (Jin and Gonsalves, 1998), N-isopropylacrylamide (Sun et. al., 2003a), methyl methacrylate (Sun et. al., 2003b), fluoroalkenes (Borkar et. al., 2006) have been previously reported.

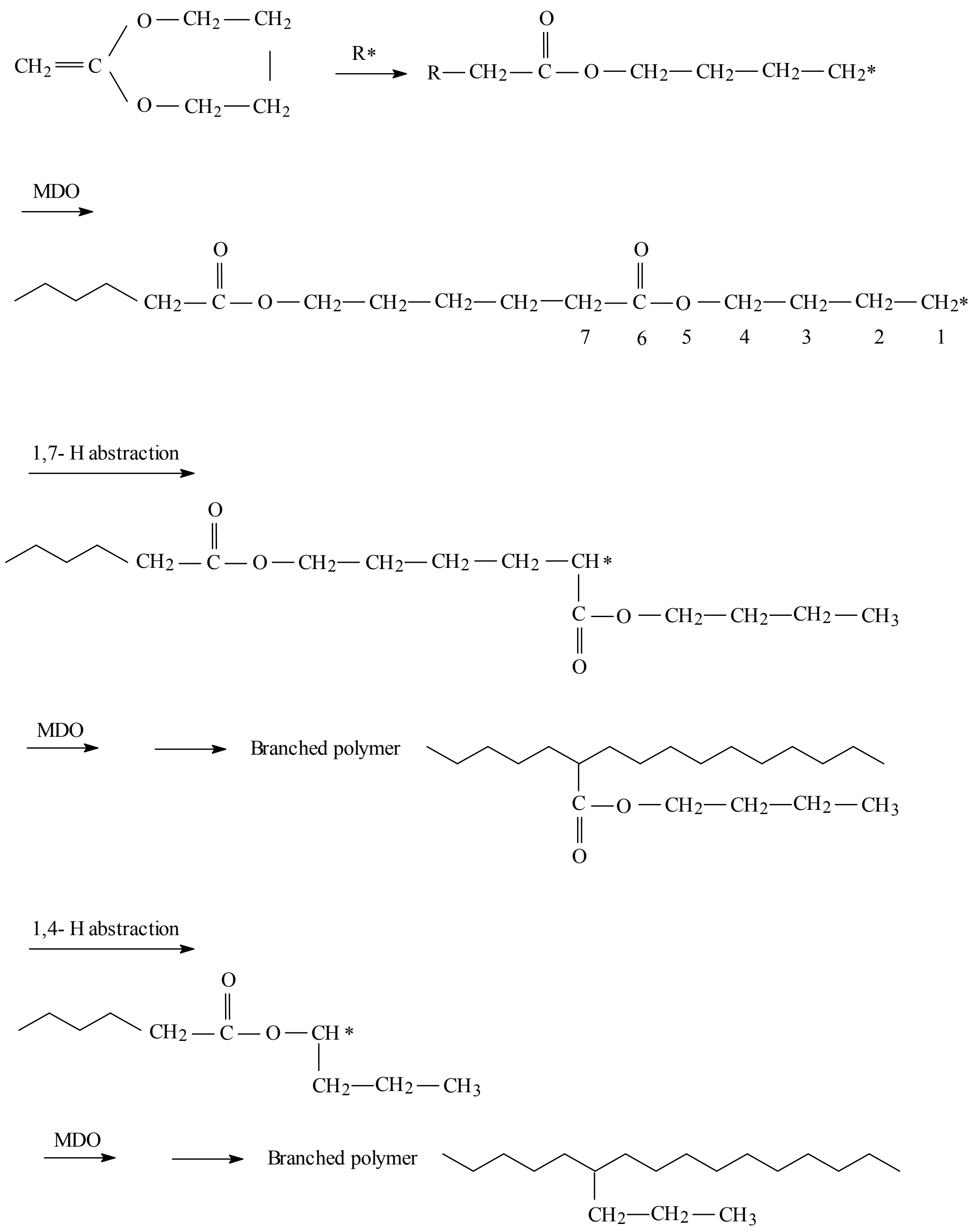


Figure 11.4 Branch formations in the free-radical polymerization of MDO (Jin and Gonsalves, 1997)

It should be noted that all the homopolymerizations and copolymerizations of MDO that have been reported in the literature were conducted at ambient pressure in bulk or in organic solvents. The use of carbon dioxide at high pressures as reaction medium for these polymerizations would not only replace the use (or reduce the use) of harmful organic solvents and undesirable catalyst residues, but also offer opportunities to incorporate the polymerization with other polymer modification processes such as particle formation and polymer foaming. However, there are no such reports so far.

In the present study, we have explored the feasibility of carrying out homopolymerizations and copolymerizations of MDO with methyl methacrylate, styrene, and acrylonitrile in supercritical carbon dioxide. The polymerization routes of these copolymerizations are shown in Figures 11.5 through 11.7. The polymers were characterized by GPC, DSC, NMR (^{1}H and ^{13}C). Additionally, the temperature, pressure, and phase separation conditions were noted during the polymerizations.

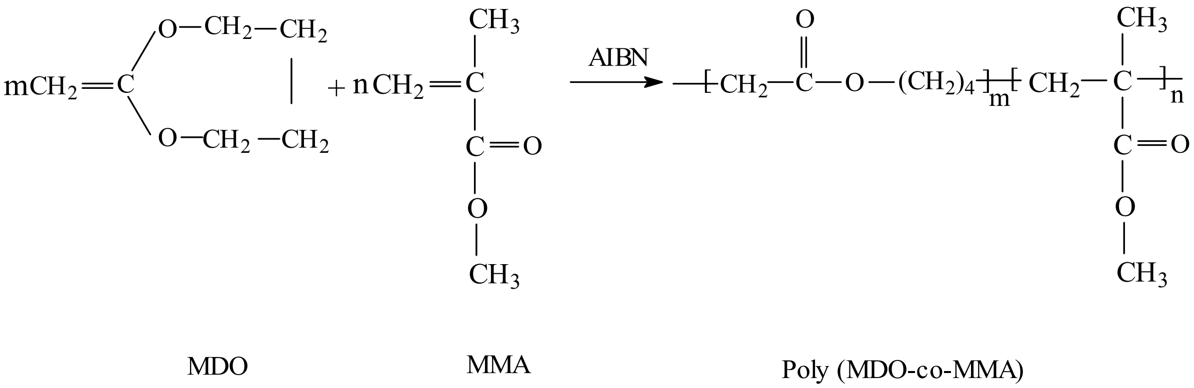


Figure 11.5 Copolymerization of MDO with MMA.

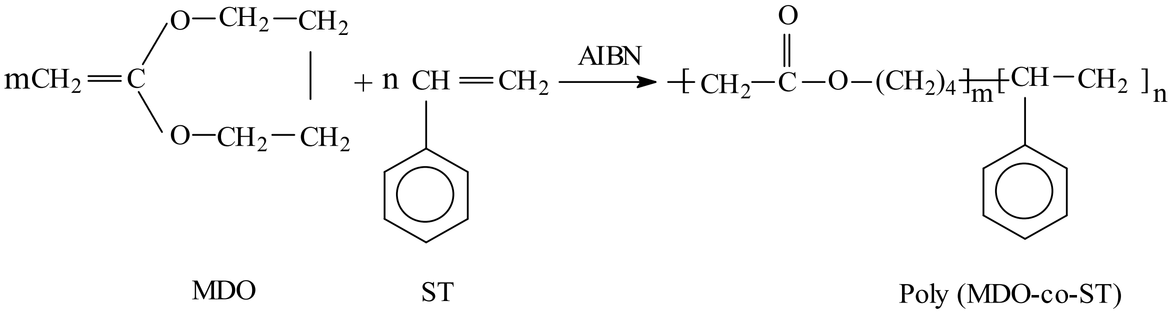


Figure 11.6 Copolymerization of MDO with ST.

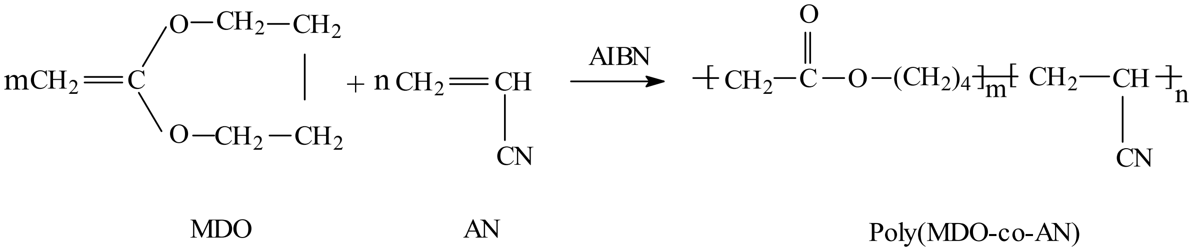


Figure 11.7 Copolymerization of MDO with AN.

11.1 Experimental

The homopolymerizations and copolymerizations of MDO were conducted in the view-cell system, which was described in Chapter 4. The monomer and the initiator AIBN were first loaded into the view cell. Then, the view-cell was closed, and the solvent carbon dioxide was charged. The temperature was raised to the target polymerization temperature. At this temperature additional carbon dioxide was charged to achieve the desired pressure. The total amount of carbon dioxide charged was noted. During the polymerization, the pressure was maintained constant by making adjustments using the pressure generator (See Figure 4.2) to move the piston. After 24 or 48 hours, the polymerization was stopped by discharging the cell. The discharge was collected. The product polymer remaining in the view cell was washed out three times using THF as solvent. The discharge and washout were then combined, and were vacuum-dried at room temperature for 72 hours to remove the THF. The samples were then further dried at a higher temperature (363 K) in a heated vacuum oven for 4 hours prior to characterizations by GPC, DSC and NMR.

11.2 Results and Discussion

11.2.1 Homopolymerization of 2-methylene-1,3-dioxepane (MDO)

The homopolymerizations of MDO in carbon dioxide were conducted at the nominal temperatures of 323 and 343 K and at pressures up to 42 MPa using AIBN as initiator. Additionally, a bulk polymerization at 323 K and ambient pressure was also conducted for comparisons. Polymerization conditions, observations on the polymer formed, and polymer molecular weight and polydispersity from the GPC tests are provided in Table 11.1.

A. Observations. Temperature, pressure, and transmitted light intensity were recorded during full duration of these polymerizations. Figure 11.8 shows this during polymerization of polymerization No. 2 (in Table 11.1). The figure provides the full record for the whole polymerization process history, including the initial stage where the temperature and pressure are increased to the target T and P in the view-cell, the progress of polymerization, and the ending stage of polymerization (displayed by decreasing pressure and temperature). As shown, during the total polymerization time from 10,000-85,000 seconds (160-1250 min) the temperature and pressure were stable at 324 K and 30 MPa. However, the transmitted light intensity underwent a sharp decrease after the first 3000 seconds (50 min) of polymerization. This decrease in transmitted light intensity arises from polymerization-induced phase separation. The phase separation was further confirmed by direct visual observations through the sapphire windows of the view-cell. After the onset of the phase separation, the polymerization mixture consists of two liquid phases, a less viscous phase at the top and a more viscous phase at the bottom of the cell. Phase separation in polymerizations carried out in fluids that are not solvents for the product polymer is an expected phenomenon. Precipitation polymerizations in carbon dioxide may result in formation of a solid polymer phase in case of polymer can crystallize. The presence of the bottom liquid phase here is viewed to be due to the relatively high polymerization temperature as compared to the glass transition temperature (T_g) of PCL which is further reduced in the fluid. The solid formation is not expected since MDO polymerizations lead to branching with little possibility for crystallization.

B. Characterization of the homopolymers. Polymerization No. 1 did not lead to measurable polymer formation. The initiator used turned out to be insufficient. Polymerization No. 4 that was carried out at ambient pressure led to only a viscous liquid. This is similar to observations reported in the literature (Jin and Gonsalves, 1997, 1998; Sun et. al., 2003a; b). The GPC evaluation of polymer No. 4 showed an elution time which was longer than that of a polystyrene standard with a molecular weight 1,200. This polymerization at ambient condition led to oligomer formation with low molecular weights.

Compared to polymerization No.1, in polymerizations No. 2, initiator amount was increased and the monomer concentration was doubled, while holding the other parameters the same. The result was a viscous liquid polymer with M_w = 25,000 and polydispersity of 1.9. Compared to the ambient pressure polymerization (polymerization No. 4, M_w < 1,200), at high pressures even using carbon dioxide as the solvent, a relatively high molecular weight polymer has thus been produced. In polymerization No. 3, the monomer concentration was the same as in polymerization No. 2 but the initiator amount was reduced, pressure was increased, and the polymerization was carried out for longer period. A polymer with molecular weight M_w = 30,300 and PDI = 1.8 was obtained. Normally, reducing the initiator concentration and increasing the polymerization time should lead to higher molecular weight. What is significant here is the effect of pressure. At high pressures, higher molecular weight polymers are formed. This is the first report on formation of high molecular weight PCL from polymerization of MDO in carbon dioxide.

For polymer produced from polymerization No. 3, ^1H and ^{13}C NMR spectra ($CDCl_3$ as deutered solvent) were generated. They are shown in Figures 11.9 and 11.10. In the ^1H spectrum, the peak at $\delta = 7.3$ corresponds to the deutered solvent. The assignments of the ^1H and ^{13}C spectrums are shown in Table 11.2 (Jin and Gonsalves, 1997). In the ^1H spectra, the peak at chemical shift = 0.9 ppm is assigned to the -H atoms in $–CH_3$ groups that are far away from any functional group, which is indicative of branching. Meanwhile, the peaks in the range of 1.3-1.7 ppm are assigned to $–CH_2$ groups in the main chain. Combined with the branch mechanism discussed earlier and shown in Figure 11.4, the integrals of the NMR peak associated with $–CH_3$ and $–CH_2$ groups are used to estimate the branch density as follow:

Branch density = (Peak area of hydrogen associated with $–CH_3$ group) / (Total peak area of hydrogen associated with both $–CH_3$ and $–CH_2$ group)

Here the NMR peak area for $–CH_3$ hydrogen is found to be 1.00 and peak area for $–CH_2$ hydrogen is found to be 10.02. Then the branch density is calculated:

$$\textit{Branch density} = 1/3 \,/\, (1/3 + 10.02/10) = 0.23 \text{ or } 23\ \% \qquad \text{(Eq.11.1)}$$

A branch density of 20 % has been previously reported for the polymerization at ambient pressure (Jin and Gonsalves, 1997). The present finding shows that polymerization of MDO at high pressure produces polymer with nearly the same degree of branching. The mechanism has not been affected by pressure, even though higher molecular weights are obtained.

11.2.2 Copolymerization of MDO

The copolymerizations of MDO have been conducted with methyl methacrylate (MMA), styrene (ST), and acrylonitrile (AN) in carbon dioxide at 343 K and 28 MPa. The copolymerization conditions and the molecular weights and polydispersities of the polymers formed are summarized in Table 11.3. The total monomer concentrations were in the range 17-20 wt %. The 50/50 copolymerizations were conducted for the copolymers with the different comonomers (polymerization experiment No. 1, 5 and 6). Copolymerization with MMA were carried out at three additional monomer ratios (MDO/MMA) with the nominal values of 20/80 (polymerization No. 2); 10/90 (polymerization No. 3) and 5/95 (polymerization No. 4). The initiator amount used was around 3 wt %.

A. General observations. Figures 11.11 through 11.14 show the variations of temperature, pressure, and transmitted light intensity during copolymerizations of MDO with methyl methacrylate for comonomer mass ratio of MDO/MMA = 50/50, 20/80, 10/90, 5/95 carried out at nominal temperature of 343 K and at 28 MPa. A sharp decrease in the transmitted light intensity is observed in the time interval from 5,000-12,000 second for each of the MDO-MMA copolymerizations. These polymerizations proceed heterogeneously after about 80-200 min of polymerization time.

Figure 11.15 shows the MDO/ST = 50/50 copolymerization process. Here phase separation is observed during the 3,000-8,000 second (50-130 min) interval of polymerization. The phase separation suggests that the solubility of this copolymer is less in the solvent medium. Figure 11.16 shows the copolymerization of MDO with acrylonitrile of MDO/AN = 50/50 at 343 K and 28 MPa. In this system the transmitted light intensity showed a two stage decrease, suggesting two levels of phase separation. The first stage is observed within 5000 second (80 min), and the second stage takes place after about 20,000 second (330 min). The transmitted light intensity shows an increase at 40,000 second which could occur if the polymers were settling.

B. Characterization of the copolymers. The copolymers that formed were either viscous liquids or solids.

Copolymerizations of MDO with MMA led to polymers with molecular weights in the range from 35,000-92,000. The results are shown in Table 11.3. The molecular weighs of the copolymers increase with increasing concentrations of MMA in the feed. The polydispersities were high, in the range from 3.1-4.8. For these polymers, GPC data showed a bimodal distribution in which the faction with higher molecular weights increased with the MMA concentration in the initial copolymerization mixtures. As noted earlier, these are precipitation polymerizations that are heterogeneous and the bimodality arises from different degree of polymerization in each phase.

Figures 11.17 and 11.18 show the ^{1}H and ^{13}C NMR spectra for PMMA sample with M_w = 15,000. The assignments for the main peaks are shown in Table 11.4. The ^{1}H and ^{13}C NMR spectra of 50/50 MDO-MMA copolymerization product (polymerization No. 1 in Table 11.3) are shown in Figures 11.19 and 11.20, respectively. Combining the ^{1}H and ^{13}C spectra of PCL that were produced from high-pressure MDO polymerization in this study (Figures 11.9 and 11.10) and PMMA (Figures 11.17 and 11.18), the assignments of the main peaks were made. They are shown in Table 11.5. In the ^{1}H spectrum, peak at 4.0 ppm is assigned to the H atom in $-CH_2$ group in poly (MDO) segment and peak at 3.6 ppm is assigned to the H atom in $-CH_3$ group in PMMA segment. The composition of this copolymer has been estimated from the integrals of the $-CH_2$ group in MDO (= 4.8) and $-CH_3$ group in MMA (= 31.3). The calculated MDO molar composition in the copolymer is 18.9 %, which corresponds to 20.9 wt %.

The DSC characterizations of these four MDO-MMA copolymers were also carried out. Figure 11.21 shows the second heating scans with a heating rate of 10 K/min. The glass transition temperatures are found to be around -16, 37, 61 and 70 ºC for the copolymer formed with 50/50, 20/80, 10/90, and 5/95 MDO/MMA comonomer ratios in the initial polymerization mixtures. Figures 11.22 and 11.23 show the second heating scans for the MDO-styrene and MDO-acrylonitrile copolymers that were obtained from reaction mixtures with the initial 50/50 comonomer mass ratios. In the MDO-ST copolymer T_g is around 8 ºC and in the MDO-AN copolymer it is observed at around 27 ºC which are significantly higher than the T_g for the MDO-MMA copolymer.

There are a number of relationships available in the literature to evaluate the T_g of a copolymer from compositional information of the copolymer and the T_g's of the corresponding homopolymers. A simple relationship is the Fox equation

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \qquad \text{(Eq 11.2)}$$

where w represents the mass fraction of the comonomer units in the polymer.

Based on the compositional information of these copolymers from the NMR data, the glass transition temperature of the homopolymer PCL from MDO polymerization was estimated. In these estimations, T_g of PMMA, polystyrene, and polyacrylonitrile were taken as 373, 368, 358 K, respectively. The calculated T_g of homopolymer (PCL) based on the T_g's of 50/50 copolymers are shown in Table 11.6. A low T_g about -155 ºC is suggested. However, this value is much lower than -57 °C that has been previously reported for a PCL sample formed from MDO polymerization at ambient pressures (Jin and Gonsalves, 1997; Sun et. al., 2003).

The much lower T_g that is calculated from the NMR composition data suggests that in the copolymer the branch length may play a more significant role in lowering the T_g than in the homopolymer. It should be noted that none of the copolymers display crystalline melting peaks.

For the 50/50 comonomer reaction mixtures, the polymerizations of MDO with methyl methacrylate, styrene and acrylonitrile lead to polymers with glass transition temperatures of -16, 8, and 27 ºC with copolymer compositions with 20.9, 14.6 and 9.5 wt % MDO. The degree of insertion of caprolactone repeat units in the copolymer chain is greatest in the copolymerization with MMA. It appears that lesser amount of caprolactone units enters the chain in copolymerizations with styrene, and even lesser caprolactone units in copolymers with acrylonitrile. These observations suggest that the reactivity ratios for the MDO-comonomer pairs must be in the order

$$r\ [\text{MDO-MMA}] > r\ [\text{MDO-ST}] > r\ [\text{MDO-AN}]$$

where r is the reactivity ratio, which in copolymerizations represents the ratio of the rate constant for the growing site reacting with the same type of monomer versus the rate constant for the growing site reacting with the other monomer, $r = k_{11}/k_{12}$. In a recent study of copolymerizations of MDO with styrene at ambient pressures, a copolymer composition of 6.5 wt % MDO is reported to result from a reaction mixture with 70/30 mass ratio of MDO/Styrene (Xu et. al., 2007). This study also indicates a relatively low insertion of MDO in styrene copolymerization as presently observed.

In another recent study conducted at ambient pressures, copolymerizations of MDO with methyl acrylate (MA) have been reported (Sun et. al., 2003). The authors have reported T_g values of -59.6 ºC, -43.5 ºC, -25.6 ºC, -7.6 ºC, and 6.0 ºC for poly (MDO), poly ($MDO_{12.9}$-co-MA), poly ($MDO_{11.6}$-co-MA), poly ($MDO_{4.2}$-co-MA), and poly (MA), respectively. Using the T_g for poly (MA) and T_g's of the copolymers reported, we have estimated the T_g for the poly (MDO) using once again the Fox equation. The evaluations lead to T_g value of -133 ºC, -124 ºC, -129 ºC which are clearly different than -59.6 ºC the authors have reported, and they are more like the present evaluations for the T_g of poly (MDO). With this additional support for the low T_g of poly (MDO), using a value of $T_{g,\ MDO}$ = -155 ºC and the observed T_g's for the copolymers formed in the present study, we estimated the copolymer compositions and compared with the NMR results. They are shown in Table 11.7. The compositions evaluated from T_g values are close to the compositions determined from the NMR data.

11.3 Summary and conclusions

This study has shown that homopolymers of MDO and the copolymers with MMA, ST, or AN can be formed at high pressures in carbon dioxide. In homopolymerization of MDO, the favorable effect of pressure was clearly demonstrated. The NMR characterization of PCL that is formed by homopolymerization of MDO confirms the branch formation resulting from the free-radical backbiting in the polymerization mechanism. The polymerizations undergo phase separation early in the polymerization, demonstrating that these are precipitation polymerizations in which the polymers have low solubility in carbon dioxide at the modest pressures (~30 MPa) employed in these polymerizations.

Table 11.1 High-pressure heterogeneous homopolymerizations of MDO in CO_2

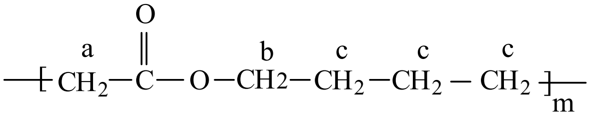
No	**Polymerization Conditions**									**Results**		
	Concentrations											
	MDO (g)	MDO (wt %)	CO_2 (g)	CO_2 (wt %)	AIBN (g)	AIBN (wt %)*	P (MPa)	T (K)	Pzn Time (hr)		M_w	PDI
1	2.02	11.2	16.1	88.8	0.0038	0.2	31.5	323	24	No product		
2	4.07	20.9	15.31	78.5	0.1136	2.8	28	323	24	Viscous liquid	25,000	1.9
3	3.90	20.6	14.98	79.1	0.057	1.5	42	343	48	Viscous liquid	30,300	1.8
4	1.06	98.6	0	0.0	0.0265	2.5	0.1	323	24	Viscous liquid	< 1,200	-

*. Concentration relative to MDO.

Table 11.2 Assignments for the ^{1}H and ^{13}C NMR spectrums for poly (ε-caprolactone) from MDO polymerization

^{1}H Spectrum

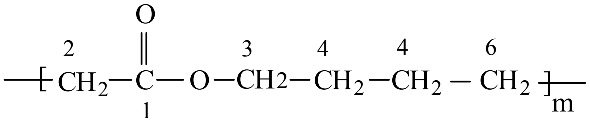
Peak	**Assignment**
δ = 4.0	b
δ =2.3	a
δ = 1.3-1.7	c (-CH_2's in main chain)
δ = 0.9	branches



$$-\!\!\left[\overset{a}{CH_2}-\overset{\overset{O}{\|}}{C}-O-\overset{b}{CH2}-\overset{c}{CH_2}-\overset{c}{CH_2}-\overset{c}{CH_2}\right]_m\!\!-$$

^{13}C Spectrum

Peak	**Assignment**
δ = 173	1
δ =64	3
δ =0-50	5 main peaks for CH_2's in main chain Many small peaks for CH_2's in branches



$$-\!\!\left[\overset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-O-\overset{3}{CH2}-\overset{4}{CH_2}-\overset{4}{CH_2}-\overset{6}{CH_2}\right]_m\!\!-$$

Table 11.3 High-pressure heterogeneous copolymerizations of 2-methylene-1,3-dioxepane (MDO) with methyl methacrylate (MMA), styrene (ST), and acrylonitrile (AN) in CO_2

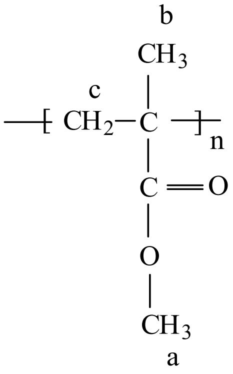
	Polymerization Conditions											Results		
	Concentrations													
	MDO (g)	MDO (wt %)	MMA (g)	MMA (wt %)	CO_2 (g)	CO_2 (wt %)	AIBN (g)	AIBN (wt %) *	P (MPa)	T (K)	Pzn Time (hr)	Product	M_w	PDI
1	1.60	9.0	1.61	9.0	14.65	82.0	0.0905	2.8	28	343	24	Viscous liquid	35,000	3.3
2	0.64	3.6	2.41	13.6	14.61	82.8	0.1046	3.4	28	343	24	White solid	50,200	4.8
3	0.33	1.9	2.71	15.3	14.70	82.4	0.0915	3.0	28	343	24	White solid	64,600	4.6
4	0.16	0.9	2.87	16.2	14.66	82.9	0.0911	3.0	28	343	24	White solid	91,500	3.1
	MDO (g)	MDO (wt %)	ST (g)	ST (wt %)	CO_2 (g)	CO_2 (wt %)	AIBN (g)	AIBN (wt %)						
5	1.59	9.0	1.55	8.8	14.50	82.2	0.0894	2.8	28	343	24	Yellow solid	6,500	1.4
	MDO (g)	MDO (wt %)	AN (g)	AN (wt %)	CO_2 (g)	CO_2 (wt %)	AIBN (g)	AIBN (wt %)						
6	1.72	10.1	1.63	9.6	13.70	80.3	0.1388	4.1	28	343	24	Brown solid	15,100	2.1

* The AIBN (wt%) is relative to comonomers MDO + MMA.

Table 11.4 Assignments for the ^1H and ^{13}C NMR spectrums for PMMA sample

^1H Spectrum

Peak	Assignment
δ = 3.6	a
δ = 0.8	b



^{13}C Spectrum

Peak	Assignment
δ = 177	1
δ = 54	2
δ = 44	3
δ = 16-18	4, 5

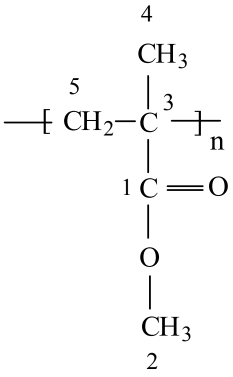
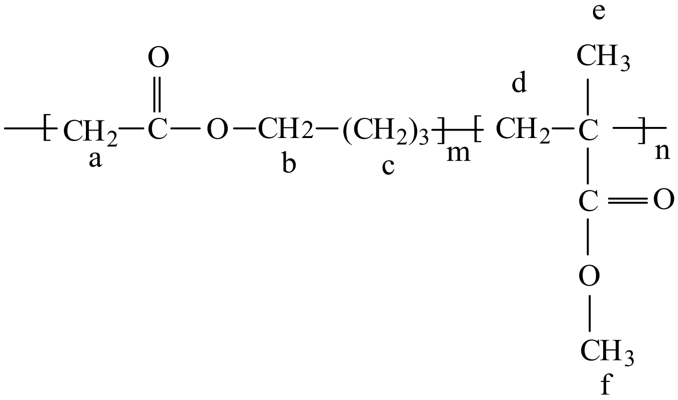


Table 11.5 Assignments for the ^1H and ^{13}C NMR spectrums for poly (MDO-co-MMA) sample

^1H Spectrum

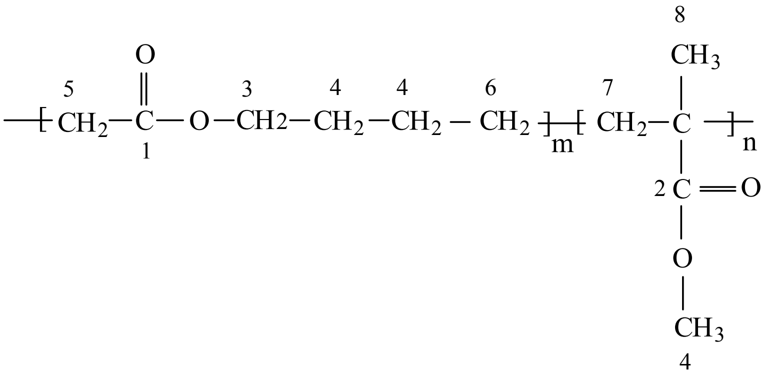
Peak	Assignment
δ = 4.0	b
δ = 3.6	f
δ = 2.0	Acetone
δ = 0.8-3.0	Too complicated to solve



$-[CH_2-C(=O)-O-CH_2-(CH_2)_3]_m-[CH_2-C(CH_3)(C(=O)-O-CH_3)]_n-$

^{13}C Spectrum

Peak	Assignment
δ = 177	1
δ = 170	2
δ = 64	3
δ = 51	4



$-[CH_2-C(=O)-O-CH_2-CH_2-CH_2-CH_2]_m-[CH_2-C(CH_3)(C(=O)-O-CH_3)]_n-$

Table 10.6 Estimation of the T_g of PCL from MDO polymerization

Comonomer ratios in reaction mixtures	MDO weight fraction in the copolymer from NMR data	Observed T_g of copolymer (ºC)	Estimated T_g of PCL (ºC)
MDO / MMA = 50/50	0.209	-16	-155
MDO / ST = 50/50	0.122	8	-169
MDO / AN = 50/50	0.107	27	-145

Table 10.7 Estimation of the MDO fraction in copolymers

Comonomer ratio in reaction mixtures	MDO weight fraction in the copolymer from NMR data	MDO weight fraction in the copolymer estimated from the Fox equation
MDO / MMA = 50 / 50	0.209	0.209
20 / 80	0.082	0.094
10 / 90	0.065	0.054
5 / 95	0.047	0.04
MDO / ST = 50 / 50	0.122	0.146
MDO / AN = 50 / 50	0.107	0.095

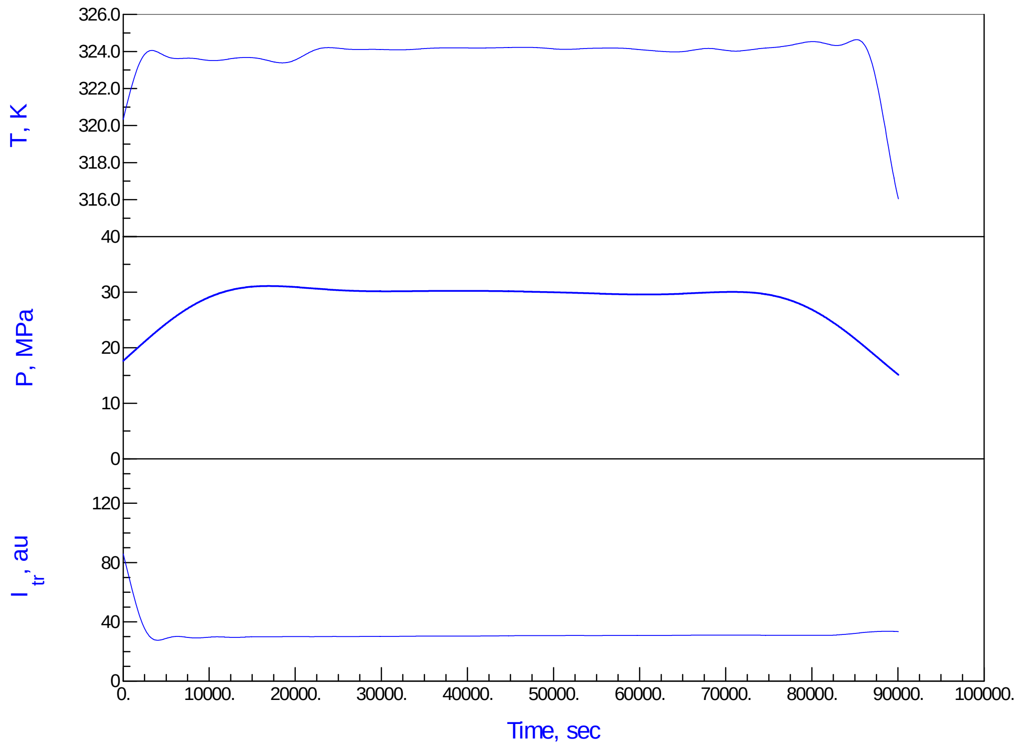


Figure 11.8 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical homopolymerizations of MDO in CO_2 at high pressure (P = 28 MPa, T = 323 K, polymerization time = 24 hrs, concentration of MDO = 20.9 wt %, and AIBN concentration = 2.79 wt %).[Polymerization # 2 in Table 11.1]

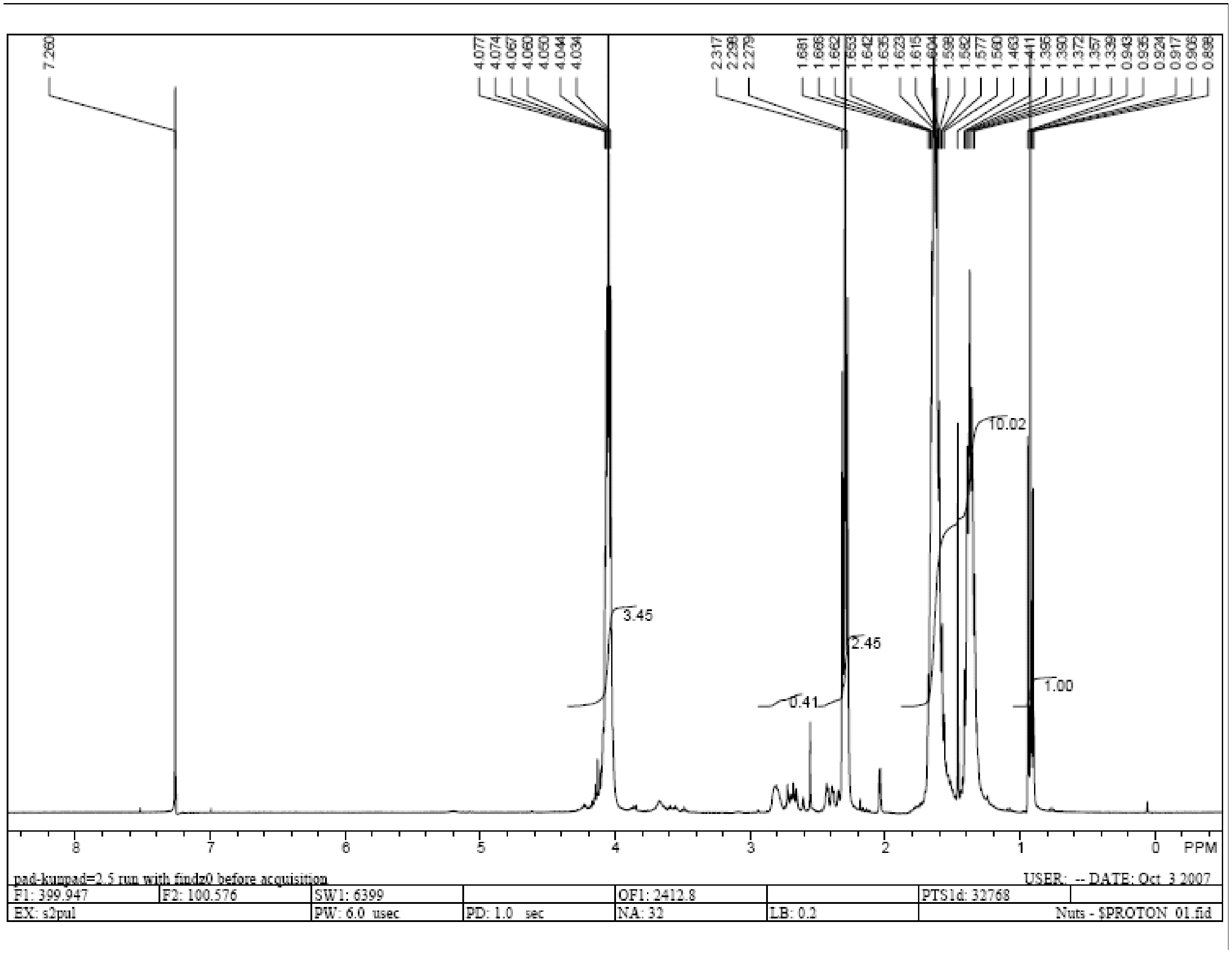


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Figure 11.9 ^{1}H NMR spectrum for PCL from MDO polymerization (No. 3 in Table 11.1).

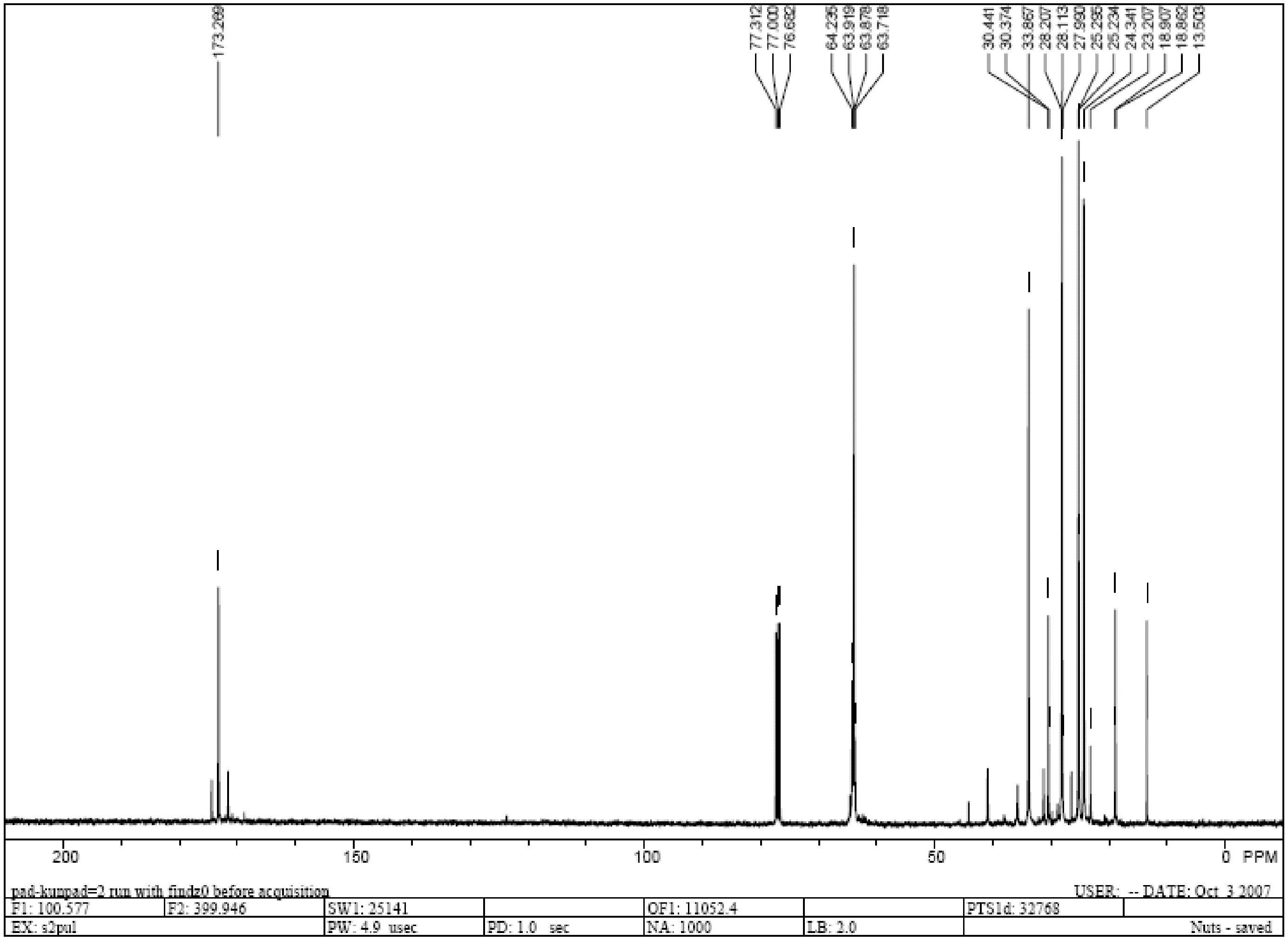

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Figure 11.10 ^{13}C NMR spectrum for PCL from MDO polymerization (No. 3 in Table 11.1).

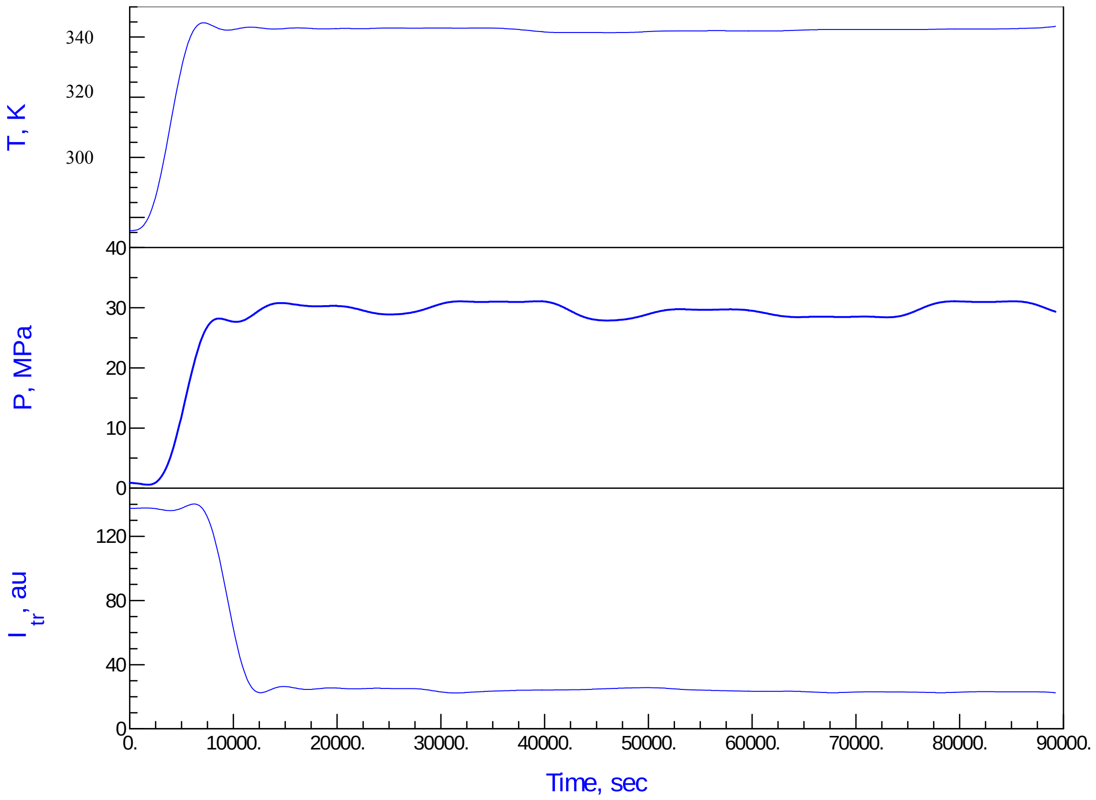

Figure 11.11 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with MMA (50/50) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 9.0 wt %, MMA= 9.0 wt %, and AIBN = 2.8 wt % (relative to amount of comonomers)) [Polymerization # 1 in Table 11.3].

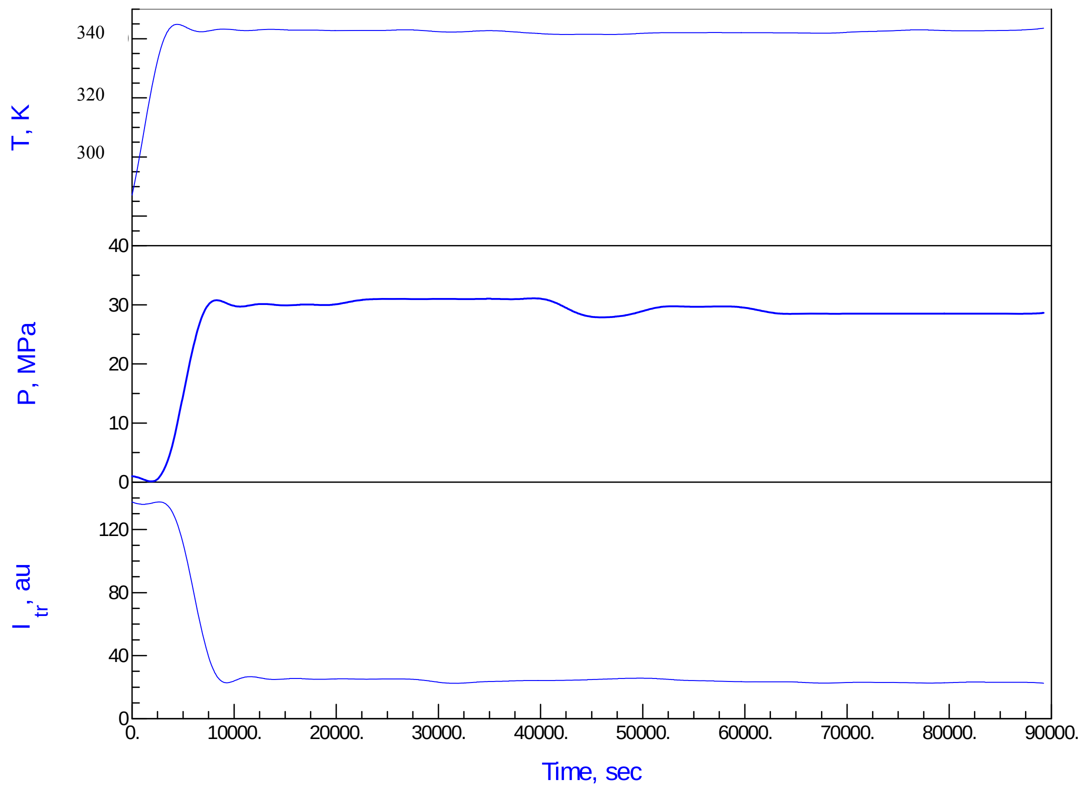

Figure 11.12 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with MMA (20/80) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 3.6 wt %, MMA= 13.6 wt %, and AIBN = 3.4 wt % (relative to amount of comonomers)). [Polymerization # 2 in Table 11.3]

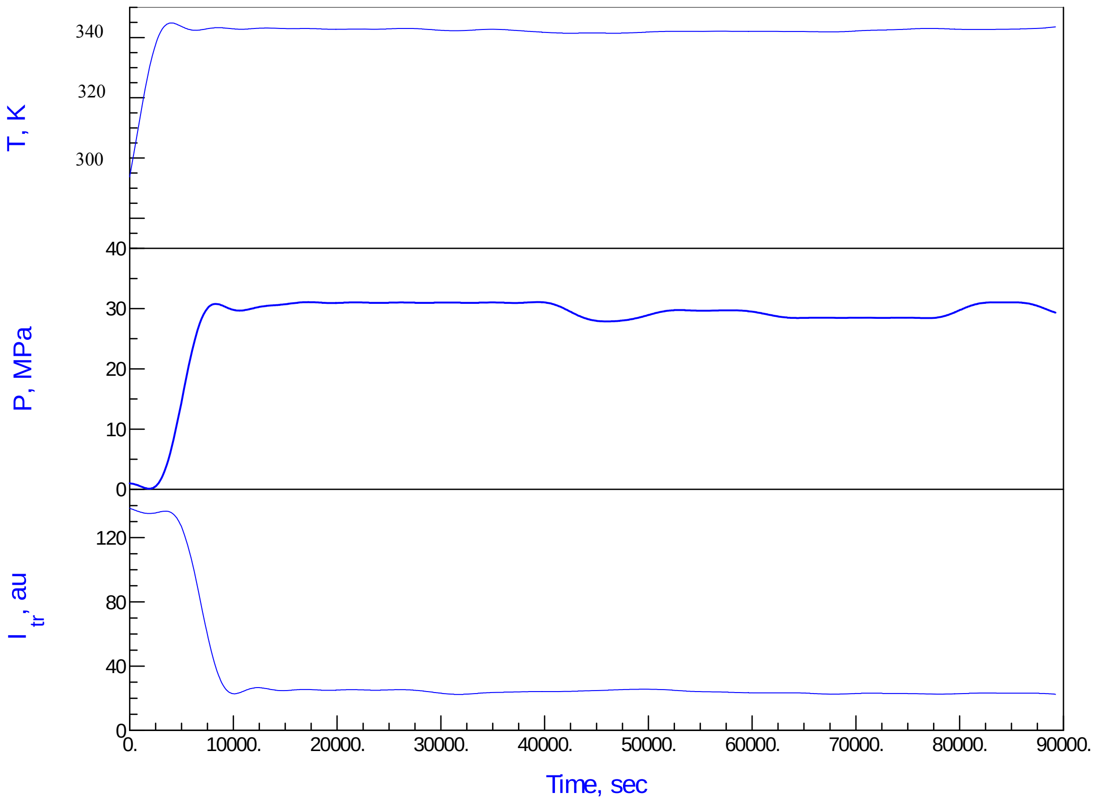

Figure 11.13 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with MMA (10/90) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 1.9 wt %, MMA= 15.3 wt %, and AIBN = 3.0 wt % (relative to amount of comonomers)). [Polymerization # 3 in Table 11.3]

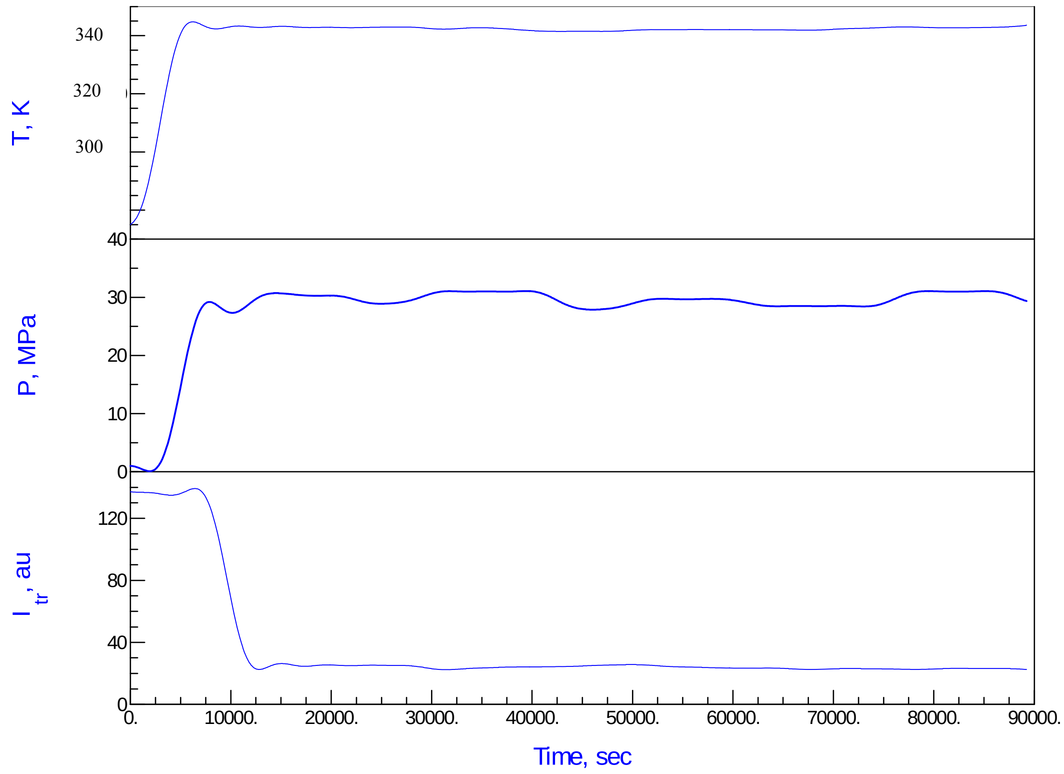

Figure 11.14 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with MMA (5/95) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 0.9 wt %, MMA= 16.2 wt %, and AIBN = 3.0 wt % (relative to amount of comonomers)). [Polymerization # 4 in Table 11.3]

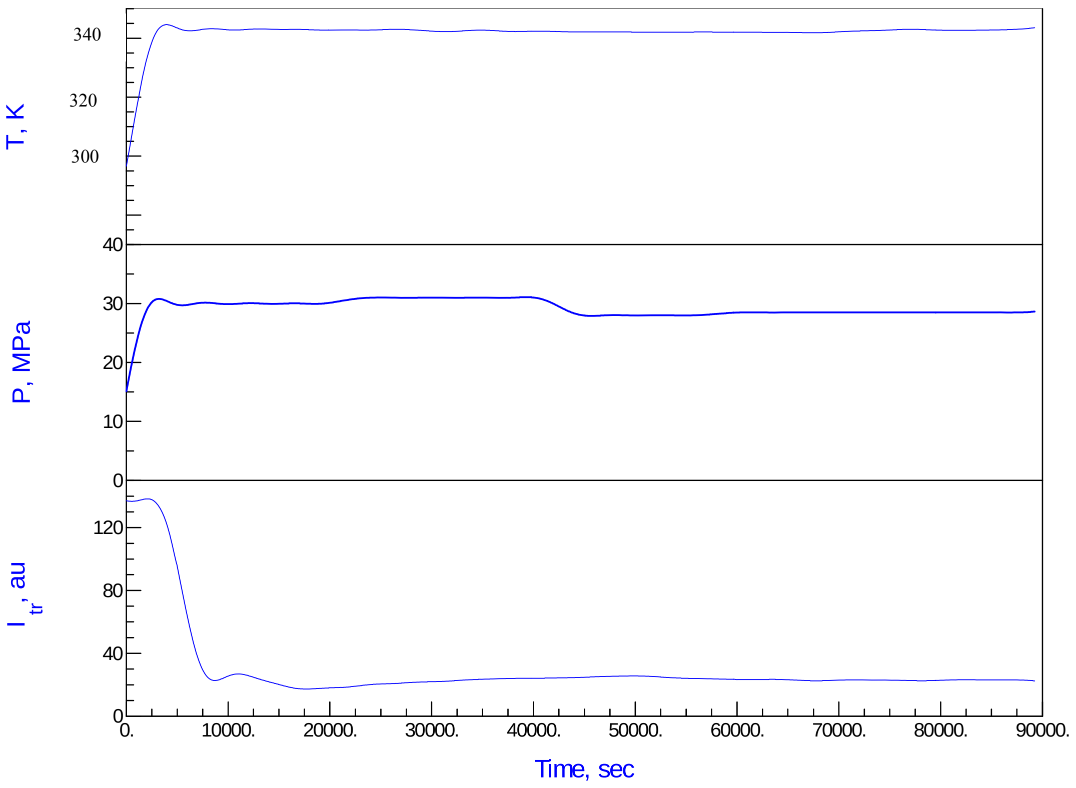

Figure 11.15 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with styrene (50/50) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 9.0 wt %, ST= 8.8 wt %, and AIBN = 2.8 wt % (relative to amount of comonomers)). [Polymerization # 5 in Table 11.3]

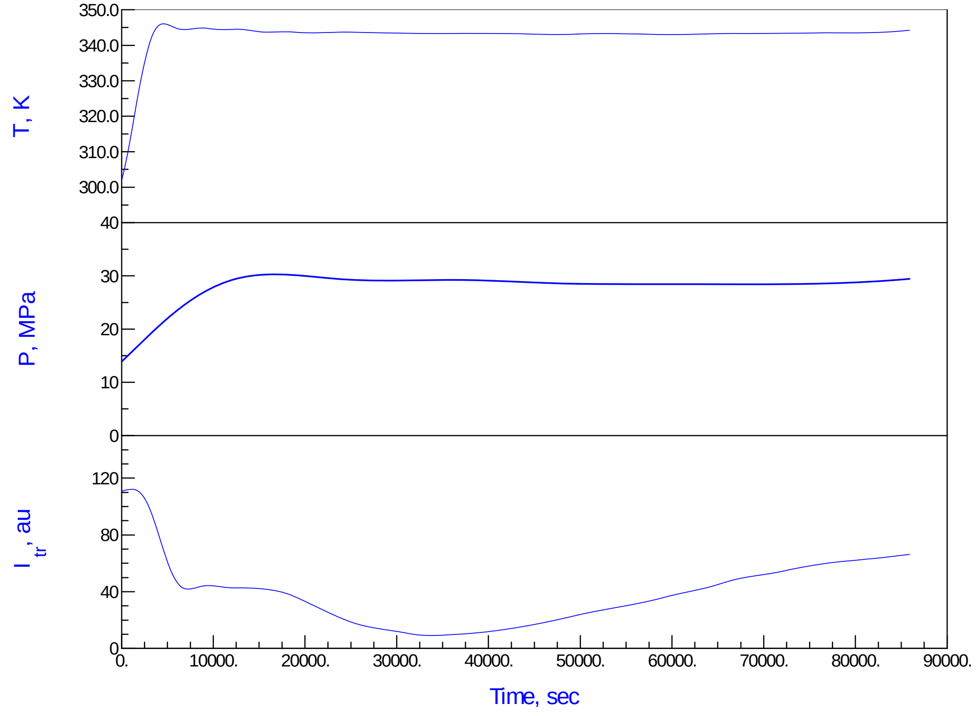

Figure 11.16 Polymerization temperature, pressure, and transmitted light intensity as a function of polymerization time for free-radical copolymerization of MDO with acrylonitrile (50/50) in CO_2 at high pressure (P = 28 MPa, T = 343 K, polymerization time = 24 hrs, concentration of MDO = 10.1 wt %, AN= 9.6 wt %, and AIBN = 4.1 wt % (relative to amount of comonomers)). [Polymerization # 6 in Table 11.3]

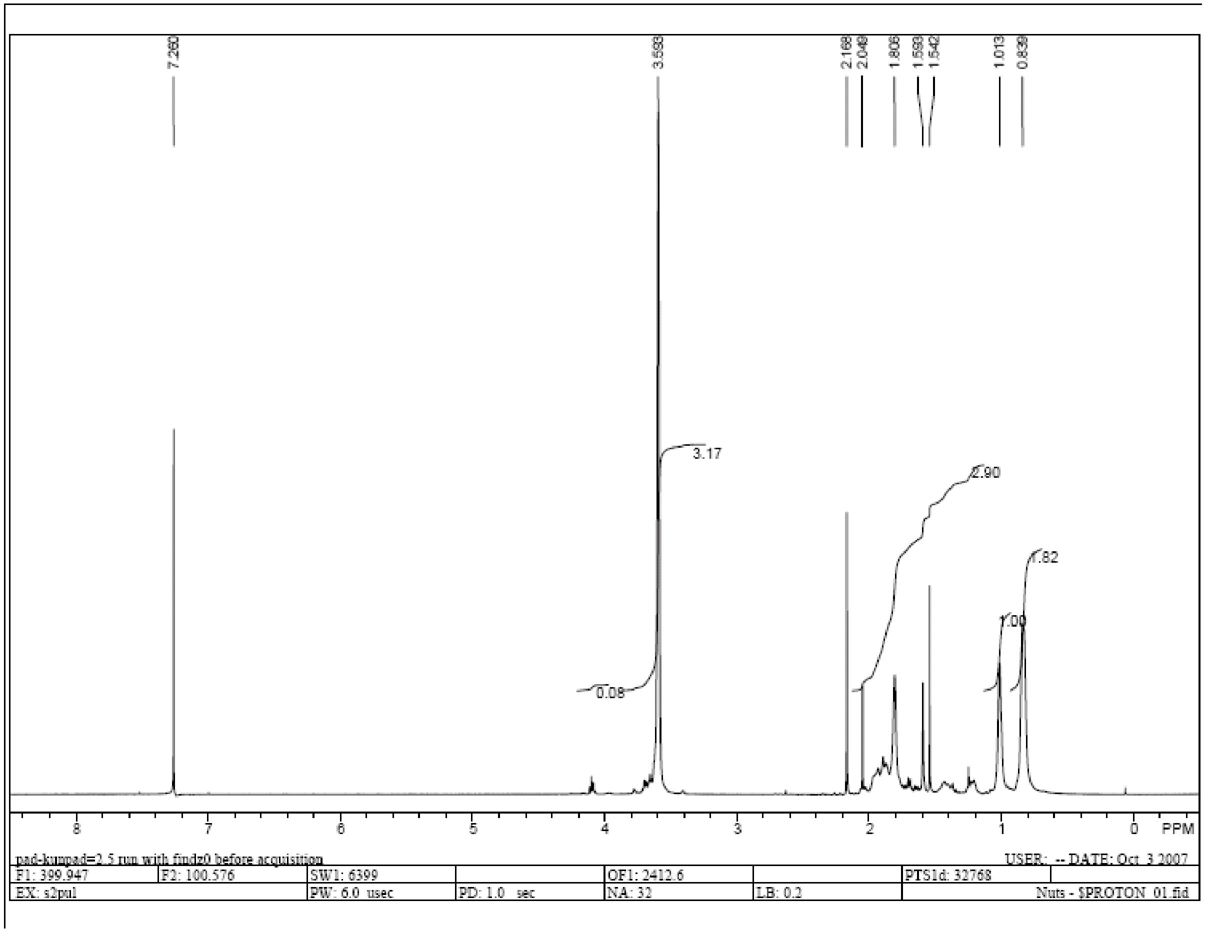

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Figure 11.17 ^{1}H NMR spectrum for PMMA.

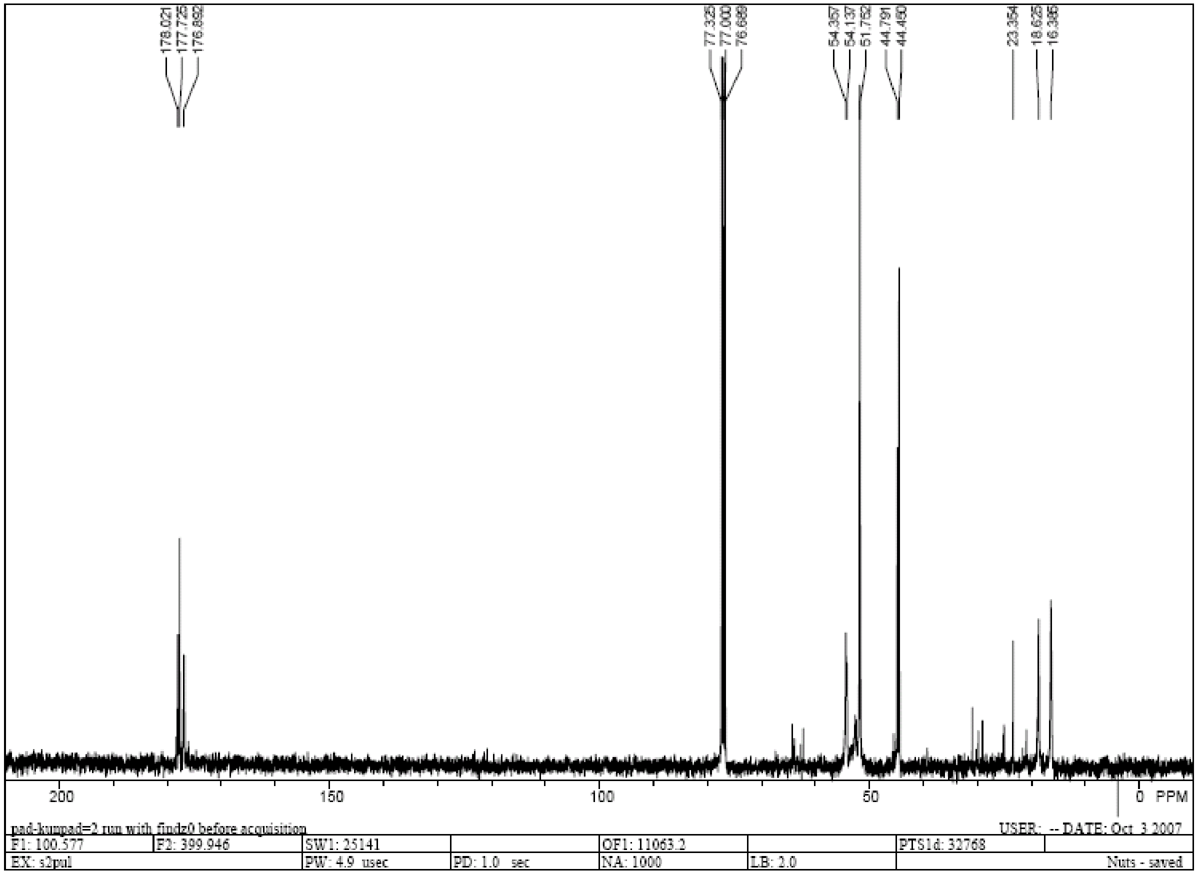

Figure 11.18 ^{13}C NMR spectrum for PMMA.

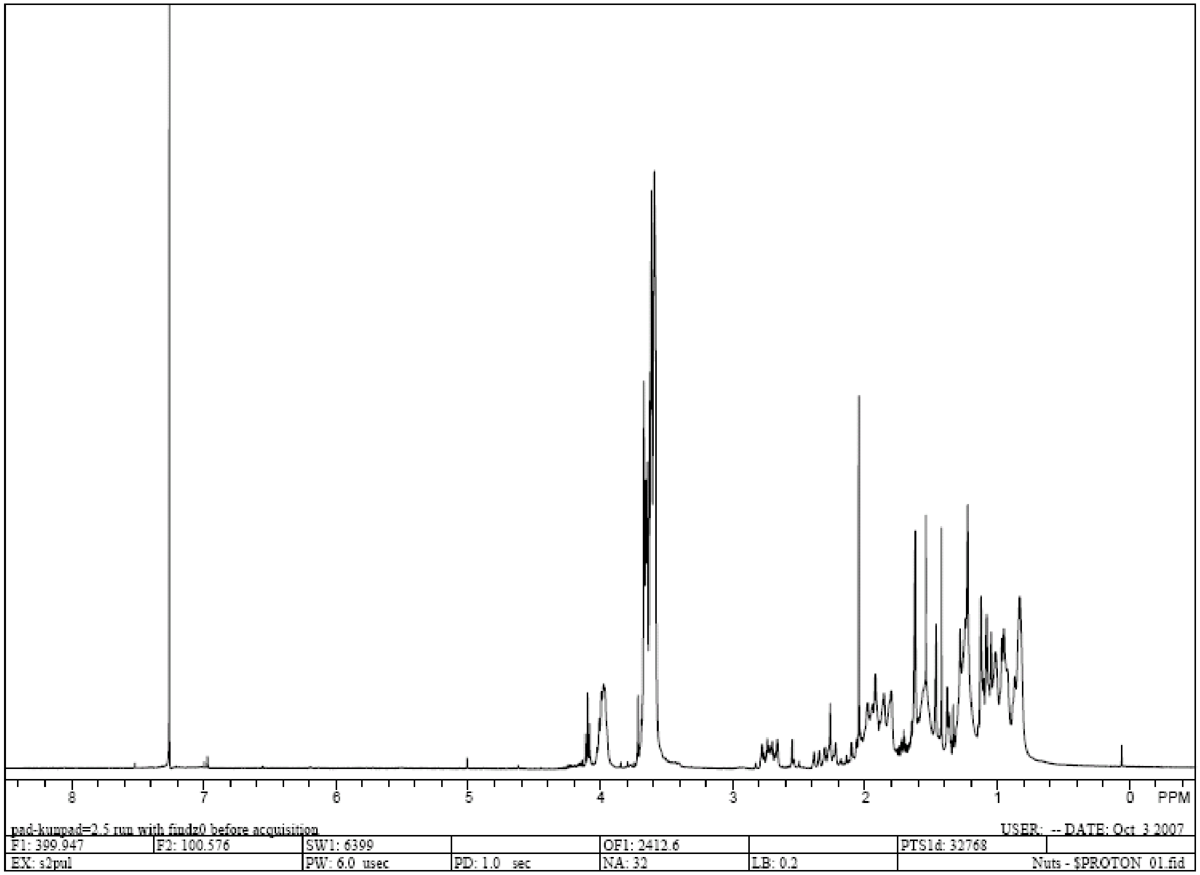

Figure 11.19 ^{1}H NMR spectrum for MDO-MMA copolymer (No. 1 in Table 11.3).

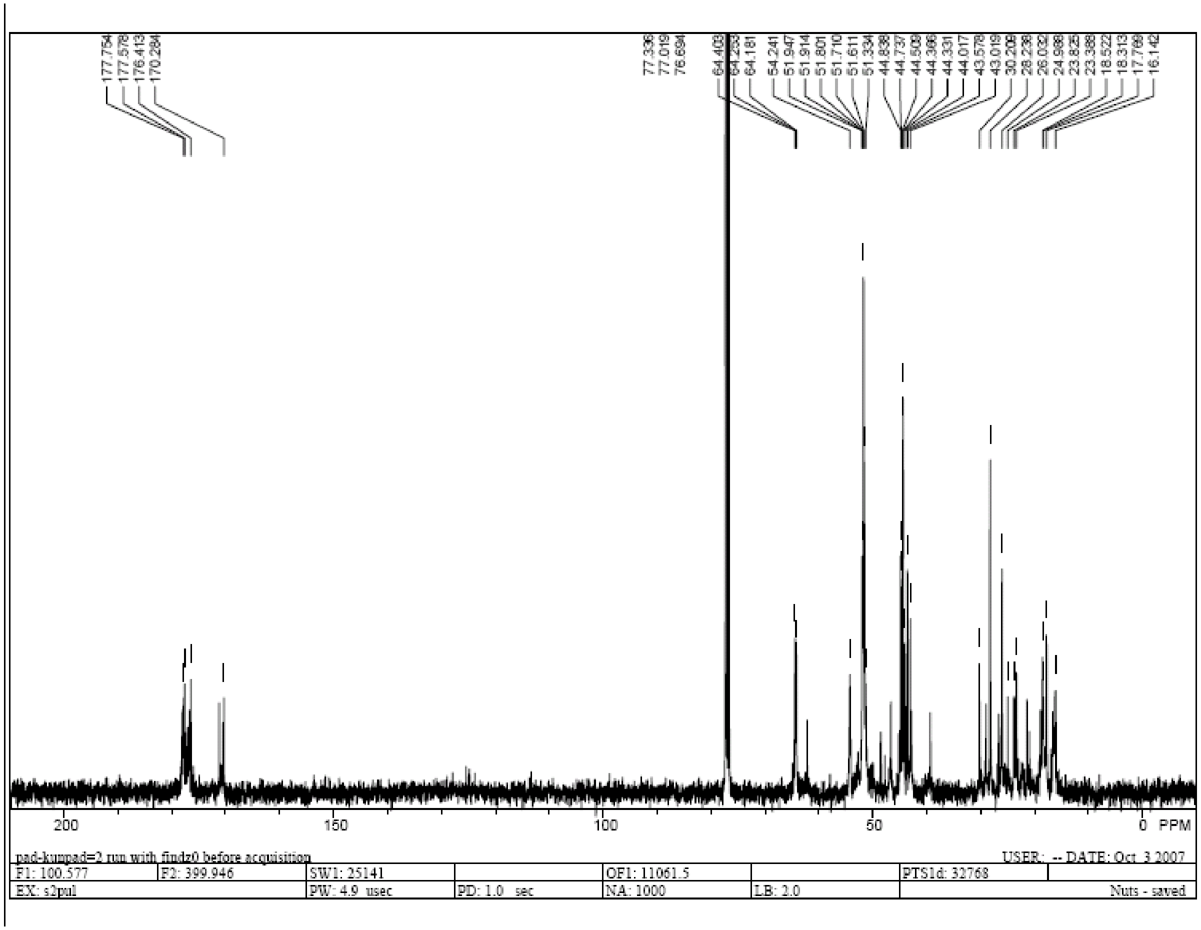

Figure 11.20 ^{13}C NMR spectrum for MDO-MMA copolymer (No. 1 in Table 11.3).

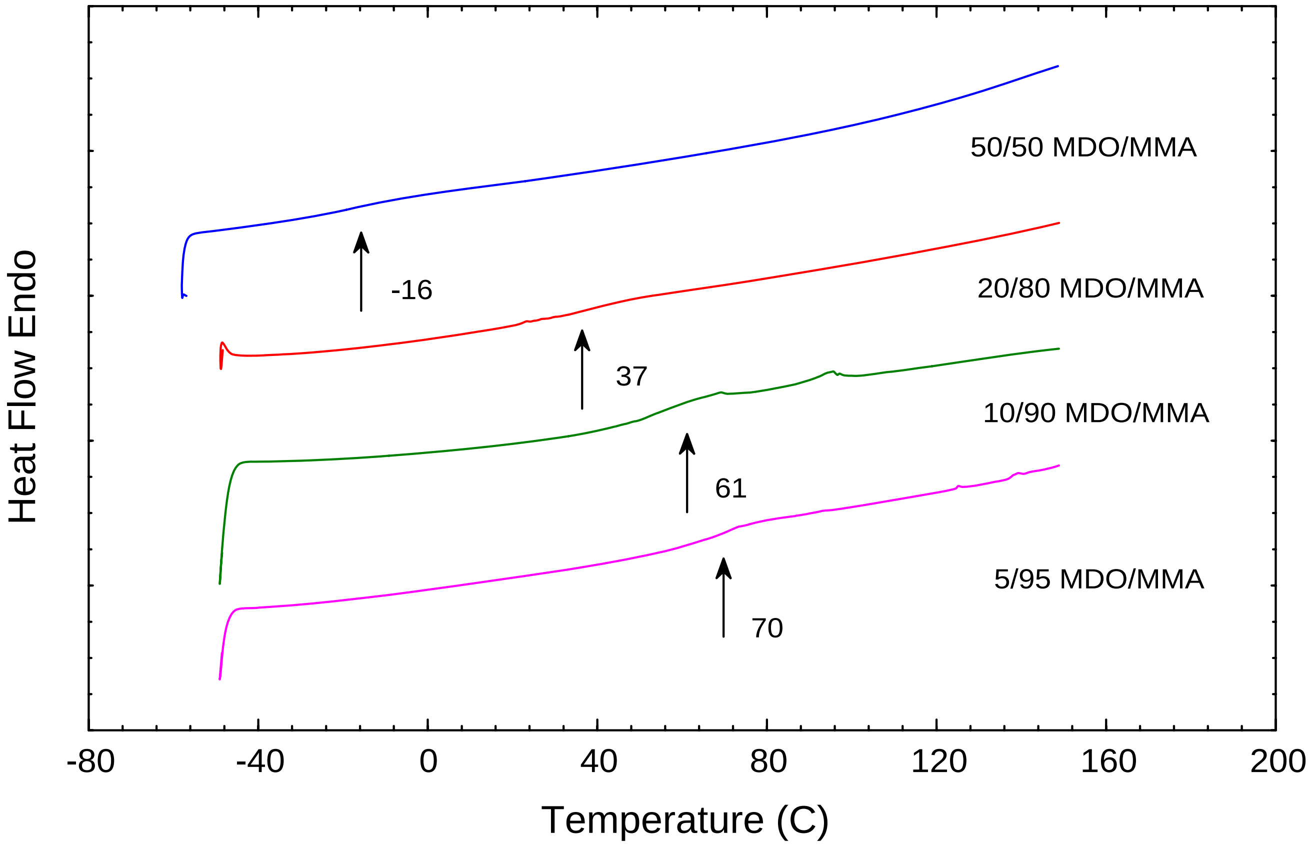

Figure 11.21 DSC tests for the 50/50, 20/80, 10/90, 5/95 MDO-MMA copolymers. The second heating scans are shown and the heating rate is 10 K/min.

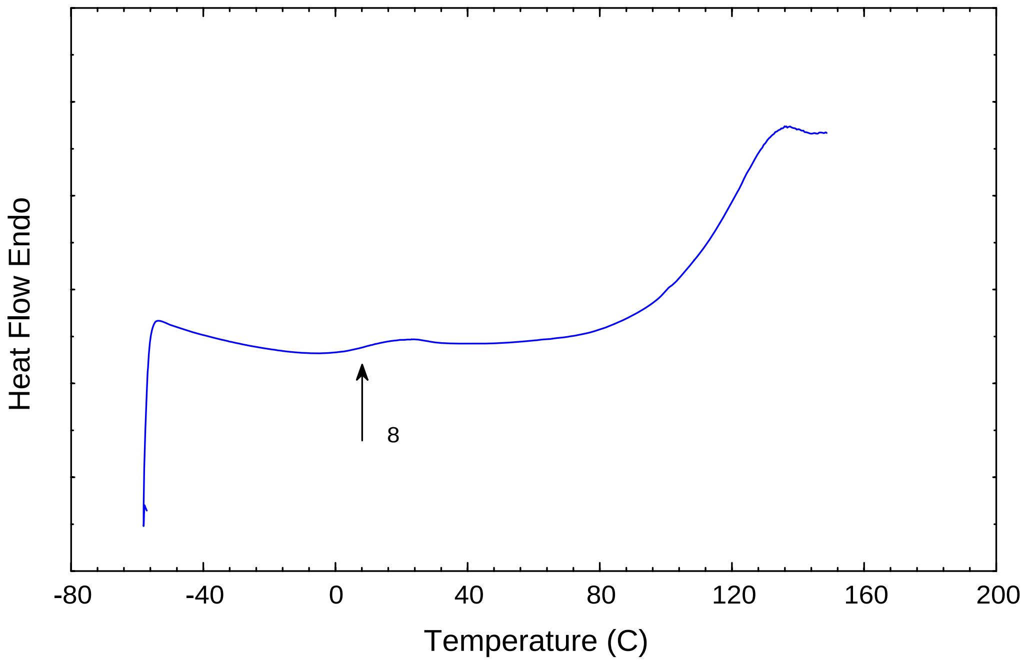

Figure 11.22 DSC test for 50/50 MDO-ST copolymer sample (No. 5 in Table 11.3).

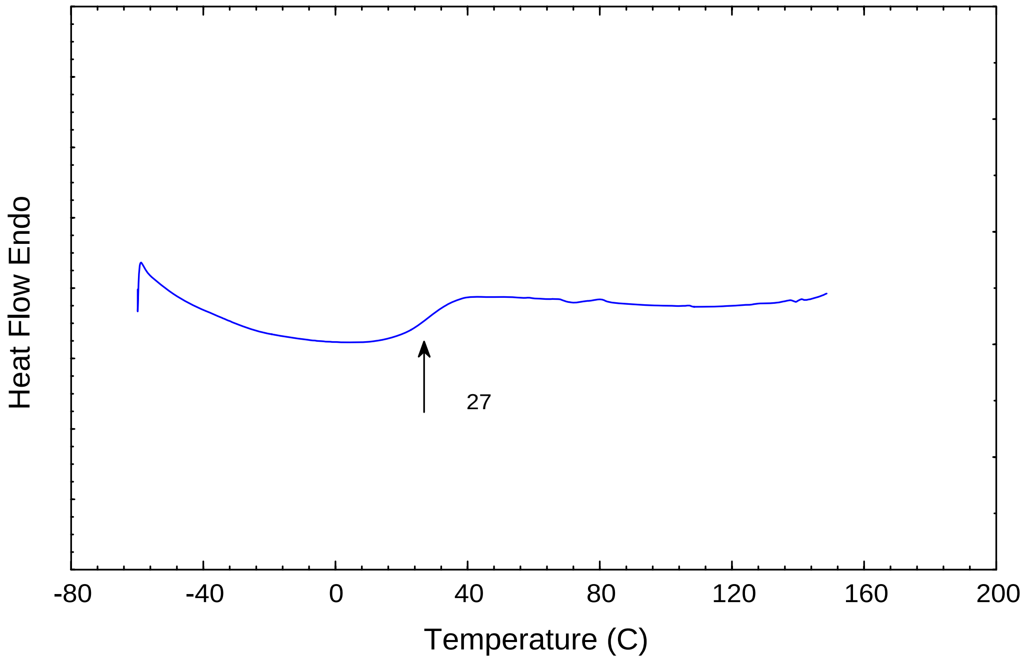

Figure 11.23 DSC test for 50/50 MDO-AN copolymer sample (No. 6 in Table 11.3).