

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Copolymerization

Suspension copolymerizations were carried out by varying initiators concentrations at three different polymerization temperatures. The results from copolymerization process showing the effects of initiators concentrations and reaction times on the percent conversions, and the relationship between polymerization pressure and polymerization time are discussed as follows.

4.1.1 Pressure-Time Profiles of 75%VCM/25%VDC Copolymers

Figure 4.1.1 demonstrates pressure-time profiles of copolymers synthesized from the monomer feed ratio of 75%VCM/25%VDC. At 30°C, with various initiator concentrations. It indicates that the pressure increased, and approached a completed similar constant with the increasing reaction time and finally decreased when the reaction is finished. The trends were also observed for other initiator concentrations for the same polymerization temperature. However, higher initiator concentration, produced shorter the constant period. This is due to the initiator dissociation along the polymerization time. The dissociate initiator reacted with monomers till all monomers were consumed, which caused the pressure to drop.

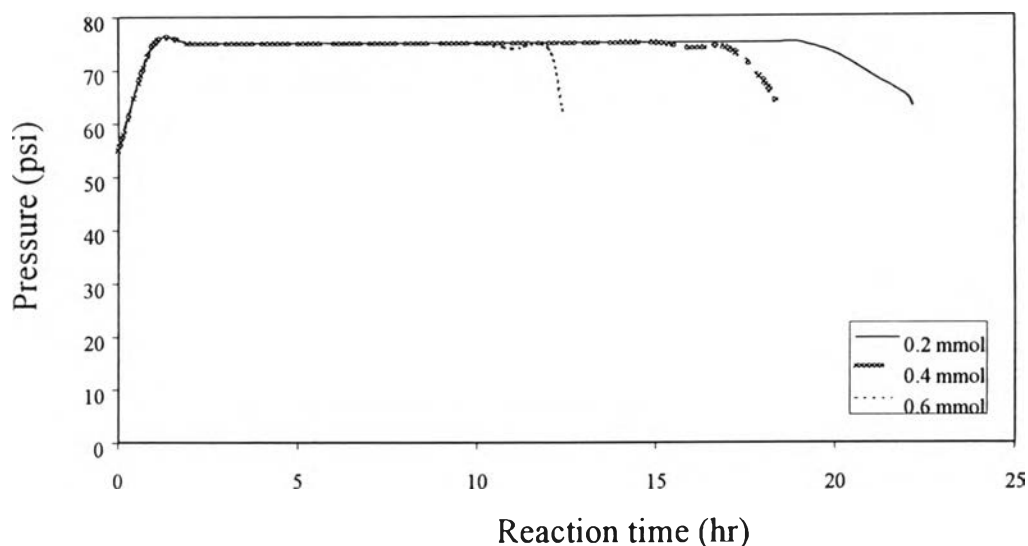


Figure 4.1.1 Pressure-time profiles of 75%VCM/25%VDC copolymers at various initiator concentrations , 30°C polymerization temperature, 0.2 phm suspending agent and 800 rpm stirring speed.

Figure 4.1.2 shows a pressure-time profiles of the same copolymers synthesized at 50°C. Similar trends were again obtained. Due to the higher polymerization temperature than the half-life temperatures of the initiators used, partial decomposition of the initiators occurred. The constant periods were therefore shorter than those conducted at 30°C.

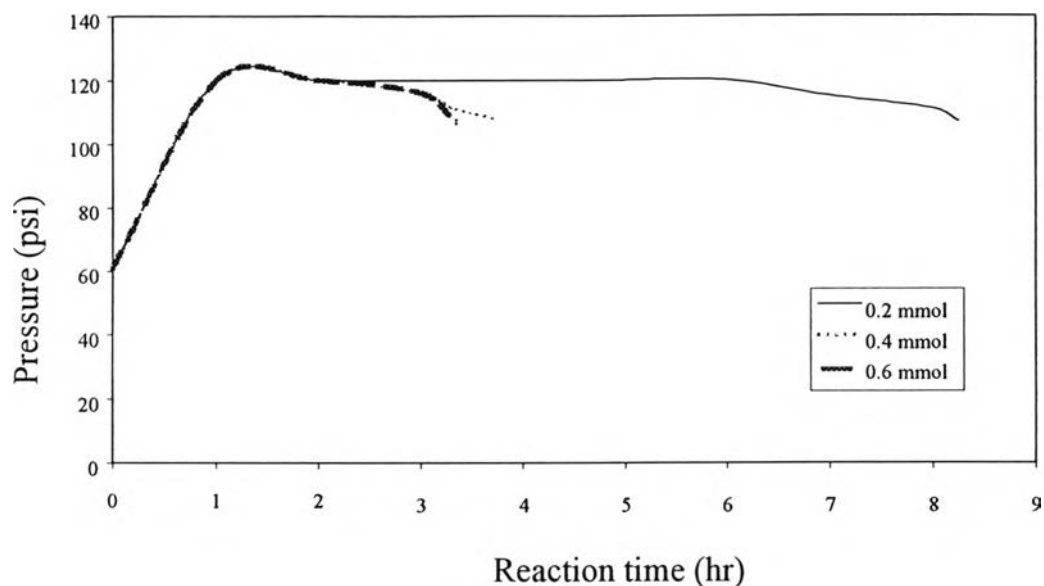


Figure 4.1.2 Pressure-time profiles of 75%VCM/25%VDC copolymers with various initiator concentration, 50°C polymerization temperature, 0.2 phm suspending agent and 800 rpm stirring speed.

Interestingly, the pressure-time profiles of the same copolymers synthesized at 65 °C, see Figure 4.1.3, shows different results. The reaction proceeded until the temperature reached 65°C, and the pressure dropped gradually. The reason is because the reaction temperature employed is much higher than the half-life temperature of the initiators. Initiator decomposition thus occurred much faster, leading to the pressure drop. This means that the polymerization temperature is too high for the initiators to withstand.

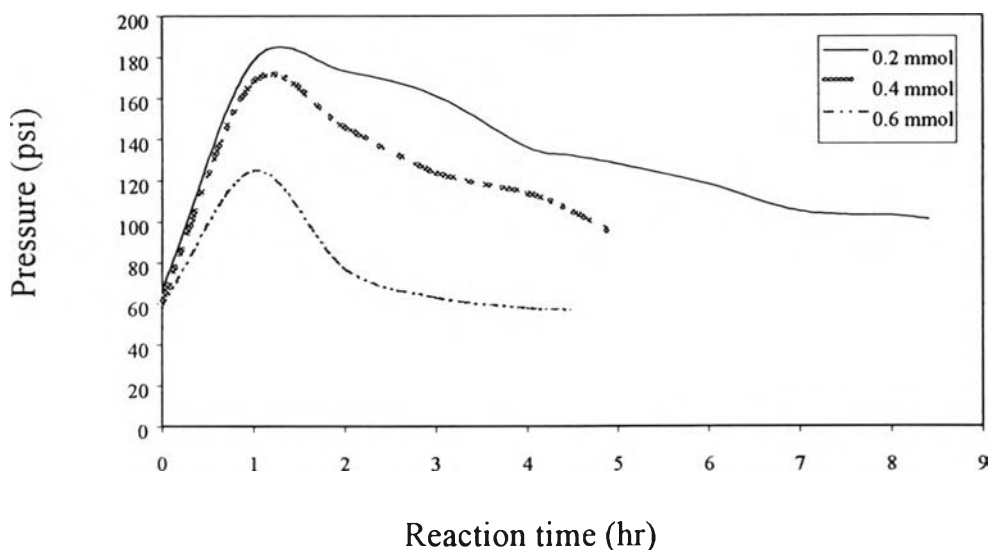


Figure 4.1.3 Pressure-time profiles of 75%VCM/25%VDC copolymers with various initiator concentrations, at 65°C, 0.2 phm suspending agent and 800 rpm stirring speed.

Figure 4.1.4 shows the relationships between initiator concentrations and reaction time. It can be observed that the smaller amount of initiator, the longer the reaction time due to the lesser amount of reactive species generated. The half-life of initiators used are 10 hr. at 44°C and 36°C. 50°C and 65°C polymerization temperatures resulted in partial decomposition of the initiators. The higher the reaction temperature, the more the decomposition occurred. As a result, there would be less initiator concentration at 65°C, the reaction time was thus longer.

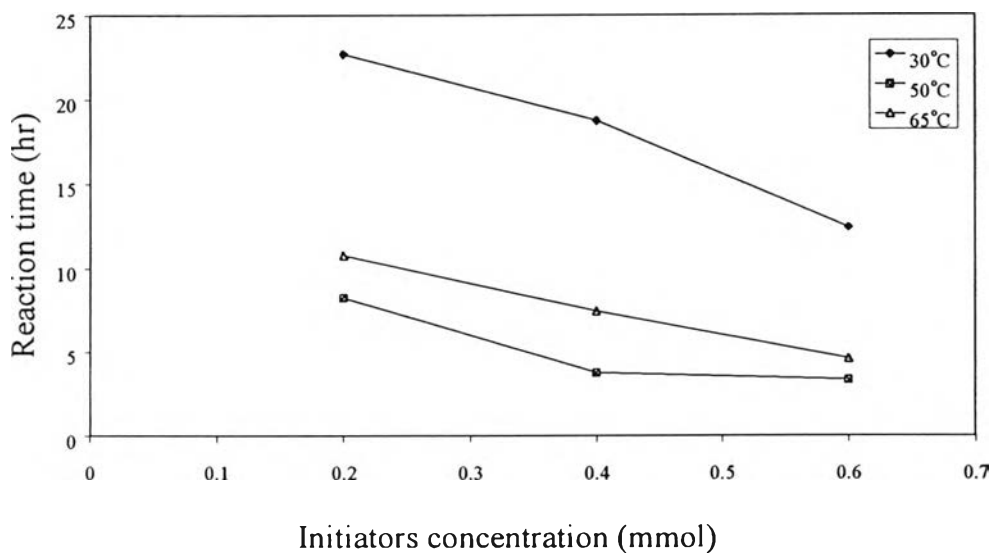


Figure 4.1.4 Relationships between initiator concentration and reaction time of 75%VCM/25%VDC copolymers synthesized at various polymerization temperatures, 0.2 phm suspending agent and 800 rpm stirring speed.

Relationship between initiator concentration and percent conversion is shown in Figure 4.1.5. Conducting the polymerization at higher temperature than the half-life of the initiators used also affects the percent conversion.

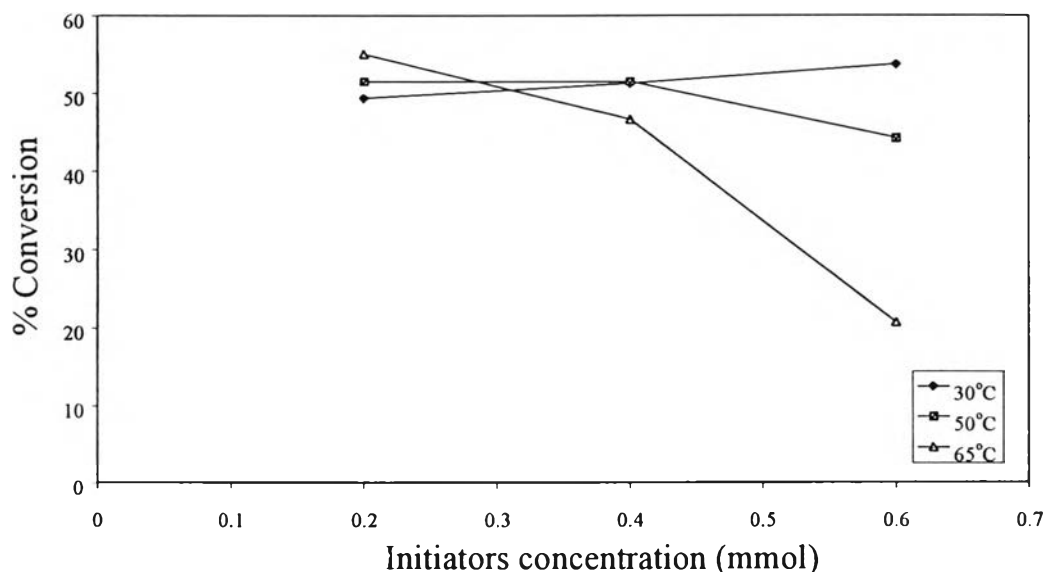


Figure 4.1.5 Relationships between initiator concentration and %conversion of 75%VCM/25%VDC copolymers synthesized at various polymerization temperatures, 0.2 phm suspending agent and 800 rpm stirring speed.

The higher the polymerization temperature, the lower the percent conversion. At 30°C polymerization temperature, the initiators gradually dissociated along the reaction time; hence, when initiator concentration increased, percent conversion increased. The more initiators, the higher percent conversion. On the contrary both polymerization temperatures of 50°C and 65°C gave lower percent conversion when the initiator concentration is increased. At 0.2 mmol initiator concentration, the initiator dissociated much faster at 65°C and 50°C, when compared with the reaction at 30°C, and this resulted in higher percent conversion. However, when the initiator concentration was higher, initiator dissociation would generate more energy. This dissociation would cause higher polymerization temperature and activate the initiator decomposition. As a result, the percent conversion decreased.

Figure 4.1.6 shows pressure time profiles of PVC and its copolymers at different compositions. It was observed that the pressure increased, approached constant value then and gradually decreased. As expected, the lower the VCM content, the longer the constant period for reaction to proceed, This imply that copolymerization took longer reaction time when the amount of VDC increased. The reason is that VDC is 10 times more reactive than VCM (reactivity ratio of VCM is 0.32 and that of VDC is 3.2).

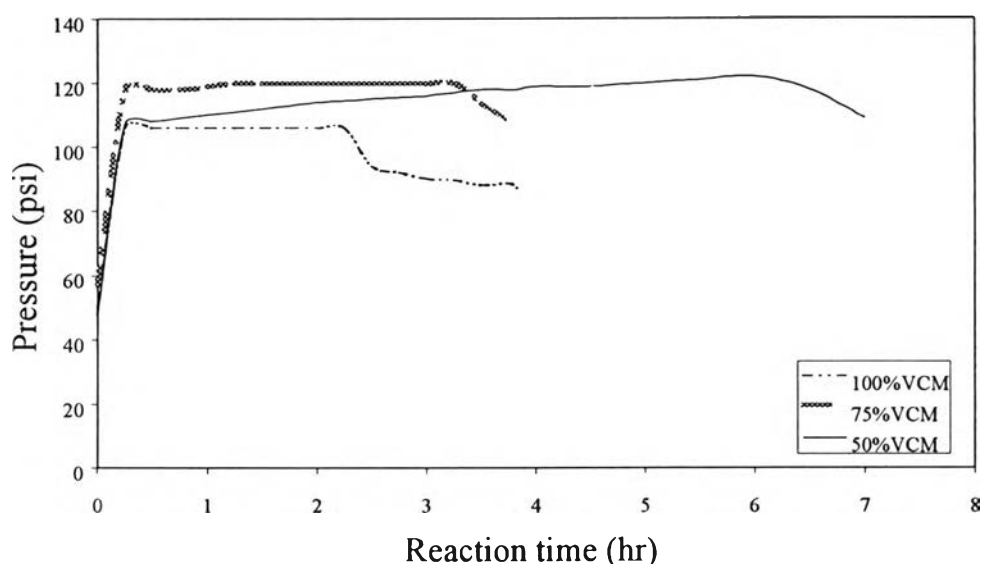


Figure 4.1.6 Pressure-time profiles of VCM/VDC copolymers at different composition, synthesized at 50 °C, 0.4 mmol initiator concentration, 0.4 phm suspending agent and 800 rpm stirring speed.

4.2 Characterization of Copolymers

4.2.1 FTIR Spectra of VCM/VDC Copolymers

FTIR spectra of copolymers with different VDC contents are compared with PVC and PVDC homopolymers (Figure 4.2.1). Four common peaks were found at 3000-2800, 1465-1450, 1300-800, and 700 cm^{-1} , corresponding to C-H stretching, CH_2 bending, C-C stretching and C-Cl stretching, respectively. The frequency region of interest falls within the range of 1200-600 cm^{-1} , since this region indicates the difference in VCM/VDC copolymer composition. The copolymer spectra obtained were almost exactly the same as that of poly(vinyl chloride). This is was not found to be surprising for the copolymers obtained from higher percentage of vinyl chloride, This is possibly due to the, large segments of the copolymer chains were PVC segments. Although the frequencies are quite similar but relative and absolute intensities are remarkably different. The characteristic peak peak of this copolymer at 1065 cm^{-1} become stronger and broader as the VDC component increased.

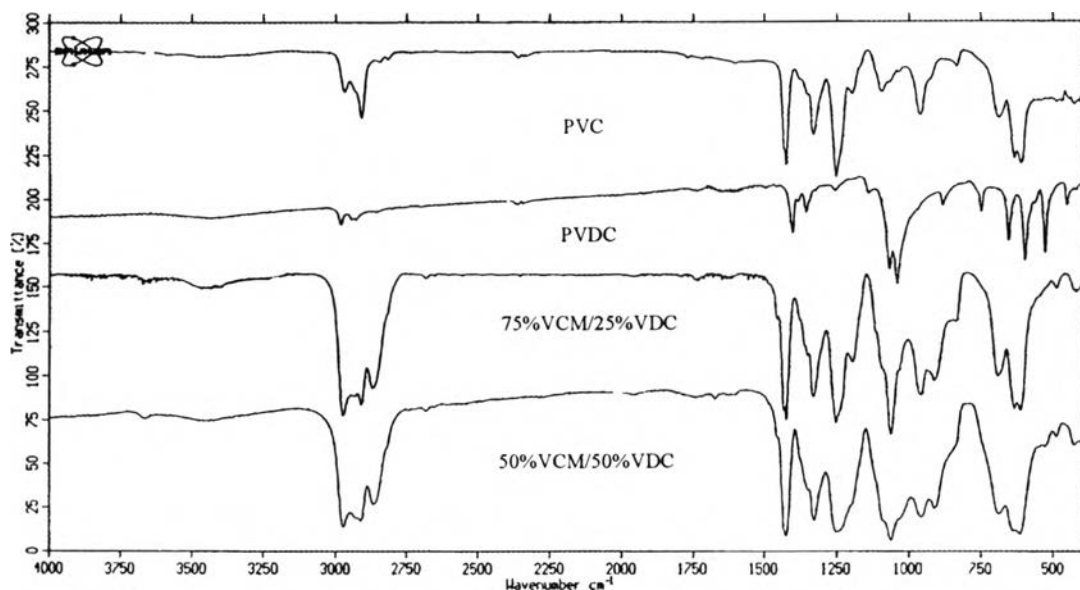


Figure 4.2.1 FTIR spectra of PVC, PVDC and its copolymers, polymerized at 50°C, 0.4 mmol initiator, 0.2 phm suspending agent and 800 rpm stirring speed.

Table 4.2.1 shows absolute and relative intensity ratios of the peaks at 1066 cm^{-1} over the peak at 960 cm^{-1} . The value of the relative intensity is more than one for all of the copolymer compositions and less than one in case of PVC. The results of the absolute intensity ratio of the polymers studied are the contrary. This observation implies that the environment in the structure of the copolymers is different from homopolymers.

Other important difference between homopolymers and copolymers observed from the FTIR spectra is the presence of the peak at 1250 cm^{-1} in the copolymer spectrum which is absent in the spectrum of poly(vinylidene chloride). This is the CH bending mode of the vinyl chloride portion.

Table 4.2.1 Absolute and relative intensities and intensity ratios of PVC, PVDC and its copolymers.

Sample	Wave no.	Abs.Inten.	Rel.Inten.	Abs.Inten. Ratio	Rel.Inten. Ratio
PVC	1066	0.715	0.106	1.164	0.385
	959	0.614	0.275		
PVDC	1069	0.287	0.102	0.529	1.729
	884	0.543	0.059		
75%VCM/ 25%VDC	1065	0.125	0.732	0.401	2.709
	960	0.311	0.272		
50%VCM/ 50%VDC	1065	0.597	0.272	0.869	2.720
	959	0.687	0.100		

4.3 ¹³C-NMR Characterization of Copolymers

As compared with the ¹³C-NMR spectra of PVC and PVDC (Figures 4.3.1 and 4.3.2), the spectrum of 75%VCM/25%VDC copolymer (Figure 4.3.3) consisted of both characteristic peaks of PVC and PVDC. A low field multiplet centered at 91.3 ppm was corresponded to VDC coupled to VCM. The peak is very weakly due to the much less amount of VDC in the copolymer. The high field multiplet centered at $\delta = 46.5$ and 57.5 ppm were belong to PVC segment. The results of splitting and shifting of the peak position implied the presence of comonomer, VDC.

When VDC was introduced in a higher ratio, the NMR spectrum showed higher intensities of VDC peaks (Figure 4.3.3). The much higher VDC content in the copolymer gives higher intensity of 2 multiplet peaks centered at $\delta = 91.5$ and 88.5 ppm which indicated VDC molecule coupled with VCM in different manner.

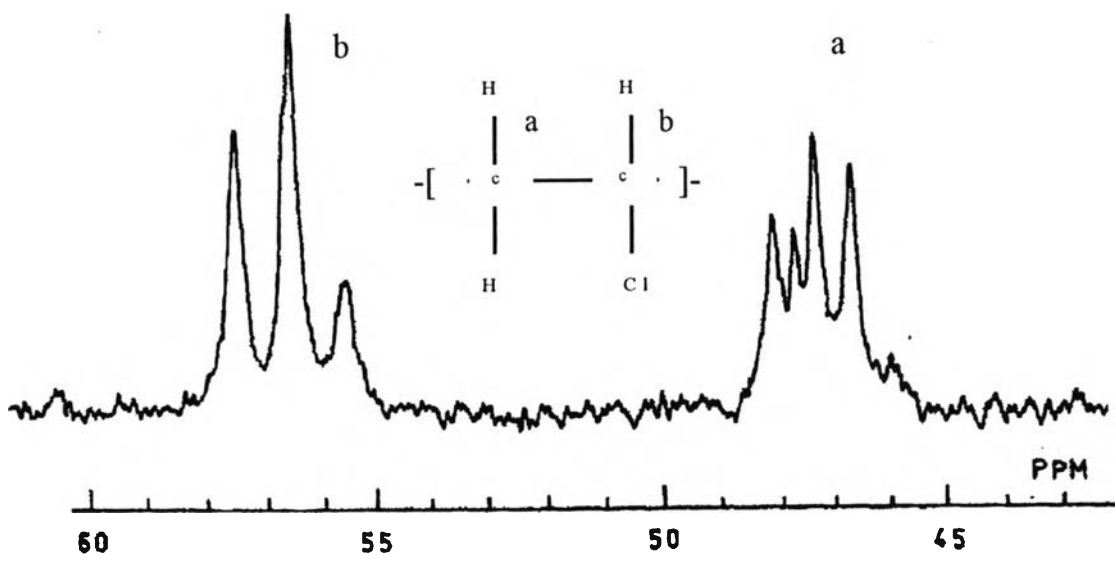


Figure 4.3.1 Coupled ¹³C-NMR spectrum of poly(vinyl chloride) (Charles, 1993)

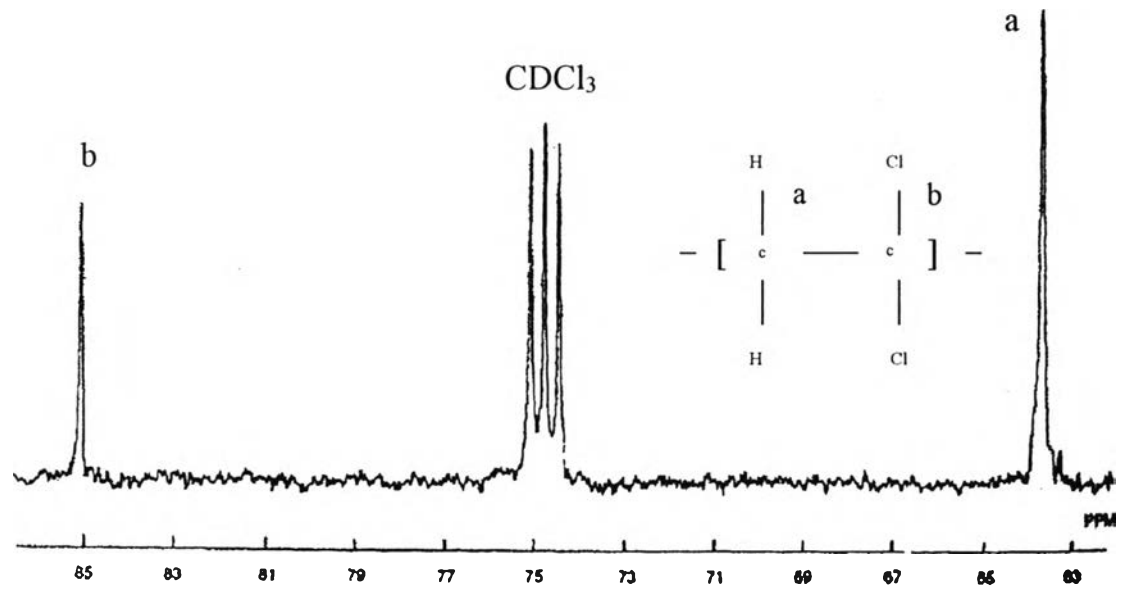


Figure 4.3.2 Decoupled ¹³C-NMR spectrum of poly(vinylidene chloride)(Charles, 1993)

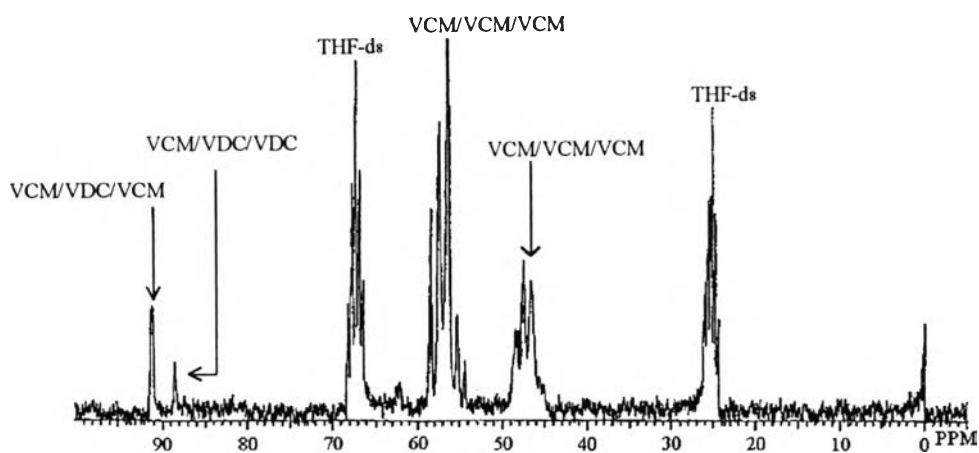


Figure 4.3.3 ^{13}C -NMR spectrum of 50%VCM/50%VDC copolymer, polymerized at 50°C , 0.4 mmol initiator, 0.2 phm suspending agents and 800 rpm stirring speed.

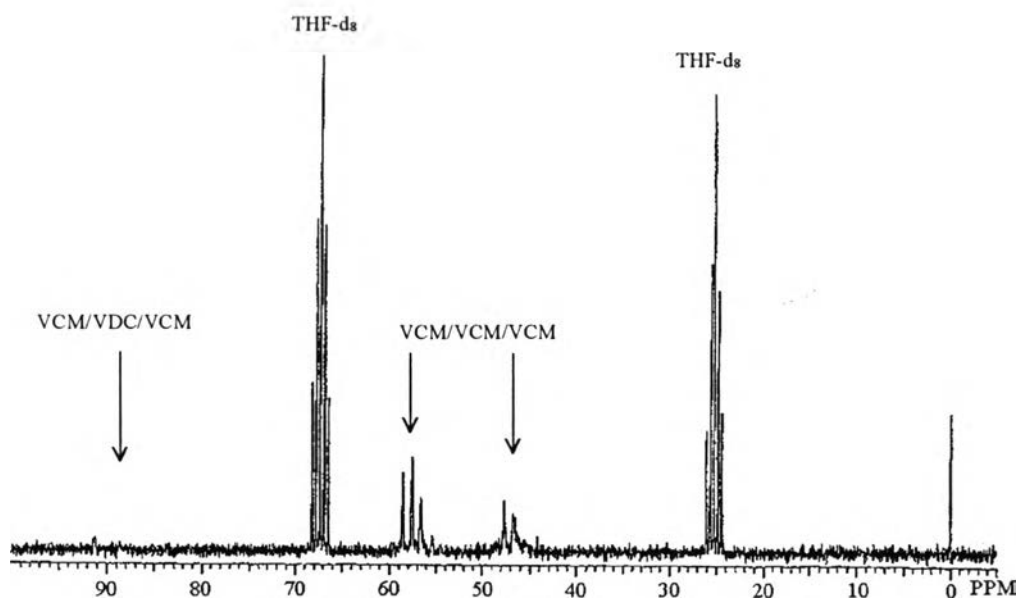


Figure 4.3.4 ^{13}C -NMR spectrum of 75%VCM/25%VDC copolymer, polymerized at 50°C , 0.4 mmol initiator, 0.2 phm suspending agents and 800 rpm stirring speed.

4.4 Thermal Behavior of VCM/VDC Copolymers

The effect of copolymer composition on melting (T_g) and glass transition (T_m) temperatures was also investigated. Using DSC technique, (Figure 4.4.1), PVC shows the T_g at 88°C whereas 75%VCM/25%VDC copolymer has T_g at 80°C . The introduction of higher VDC content, (50% VDC), led to copolymer having even lower T_g , 66°C . This was resulted from higher free volume generated by large chlorine atoms from VDC molecules. therefore the higher the amount of VDC, the lower the T_g , as summarized in Table 4.4.1.

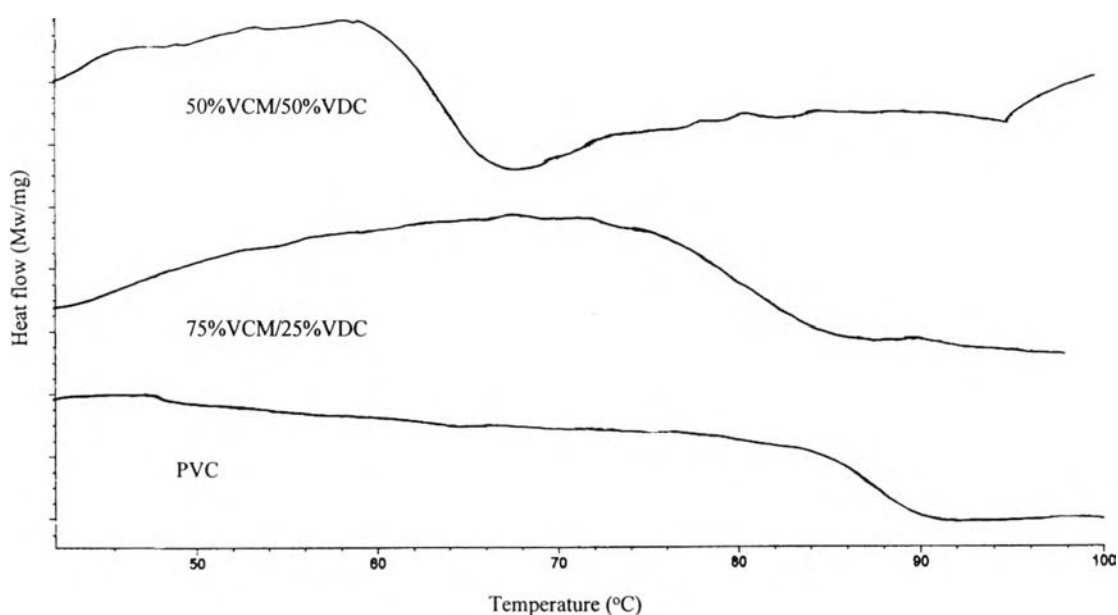


Figure 4.4.1 DSC thermograms of PVC and its copolymers, polymerized at 50°C , 0.4 mmol initiator, 0.2 phm suspending agent and 800 rpm stirring speed.

Table 4.4.1 Tg values of PVC, PVDC, and copolymers.

Polymer	Tg(°C)
PVC	88
PVDC	-17
75%VCM/25%VDC	80
50%VCM/50%VDC	62

4.5 Particle Size

Table 4.5.1 shows particle sizes of copolymers by varying the speed of stirring at a particular amount of suspending agent. It appeared that the higher speed of stirring, the smaller the particle size of the copolymers.

Table 4.5.1 Particle sizes of 75%VCM/25%VDC copolymer by variation of stirring speed at 0.4 mmol initiator, 0.2 phm suspending agent, 50°C polymerization temperature.

Speed of stirring(rpm)	Particle size(μm)
700	187
800	170
900	128

4.6 Molecular Weight

At the polymerization temperature of 30°C, which is lower than half-life temperature of the initiators, the initiator gradually dissociate along the reaction time. In the case of PVC, the higher initiator concentration, the lower molecular weight. This is due to the higher reactive species concentration creating more polymer chain. When VDC concentration increased, it allowed chain transfer reaction to occur due to the effect of its reactivity, which is higher than VCM. The molecular weight was therefore lower than those have lower VDC content. The more VDC loading, the lower molecular weight obtained, (Table 4.6.1).

At the higher polymerization temperature of 50°C, the copolymers obtained have lower molecular weight when compared with those obtained at 30°C. It was resulted from the effect of polymerization temperature of 50°C which is higher than the half-life temperatures of the initiators used. The high temperature employed caused the initiators to dissociate along with decomposition quicker and generate higher reactive species concentration which reduced the molecular weight, in case of PVC. The reduction of molecular weight of the copolymers, 75%VCM/25%VDC and 50%VCM/50%VDC were resulting from the much different reactivity of the two monomers used.

Since VDC is more reactive than VCM, a lot of short chains could occur due to the effect of chain transfer reaction. The molecular weight of 50%VCM/50%VDC was therefore lower than those with the lower VDC content, It can be concluded that both the initiator concentration and reactivity of monomers affect the molecular weight of the resulting copolymers.

Table 4.6.1 Molecular weight of PVC and VCM/VDC copolymers

Polymerization temperature(°C)	Polymers	Molecular weight	
		0.2 mmol initiators	0.4 mmol initiators
30°C	PVC	206149	171751
	75%VCM/25%VDC	102060	257549
	50%VCM/50%VDC	24663	53929
50°C	PVC	70165	60691
	75%VCM/25%VDC	68535	29065
	50%VCM/50%VDC	27449	18431

5.1 Mechanical Property Study

Figures 5.1 to 5.6 show the effect of initiator concentration on tensile properties of PVC and VCM/VDC copolymers. They indicate that tensile properties were affected by molecular weight of the polymers studied due to the much different initiator concentration used and also the effect of chain indicate transfer reaction which caused the lower of polymer molecular weight.

These figures, show that tensile properties of PVC and copolymers at 30°C were better than those polymerized at 50°C. These figures also show that PVC has the best tensile properties due to much higher molecular weight when compared with another copolymer compositions. Another mechanical results, such as stress at break of 75%VCM/25%VDC), also show the same trends due to the same effect. By comparing tensile properties of the PVC and copolymers synthesized with the commercial saran (Nikel, 1996), it appeared that the commercial one shows better percent elongation (10%) and better tensile properties (34.5-69 MPa) .

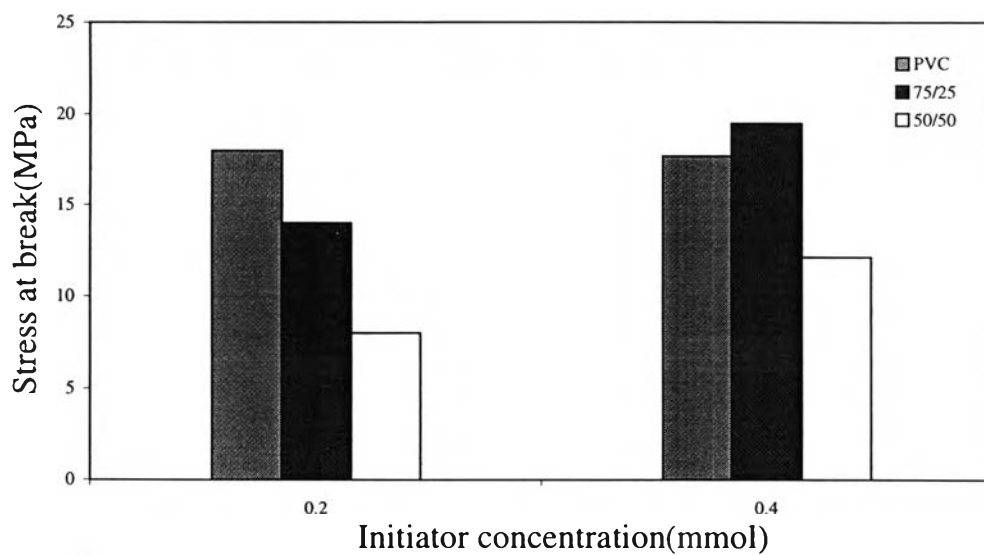


Figure 5.1 Relationships between initiator concentration and stress at break of PVC and copolymers at 30°C polymerization temperature.

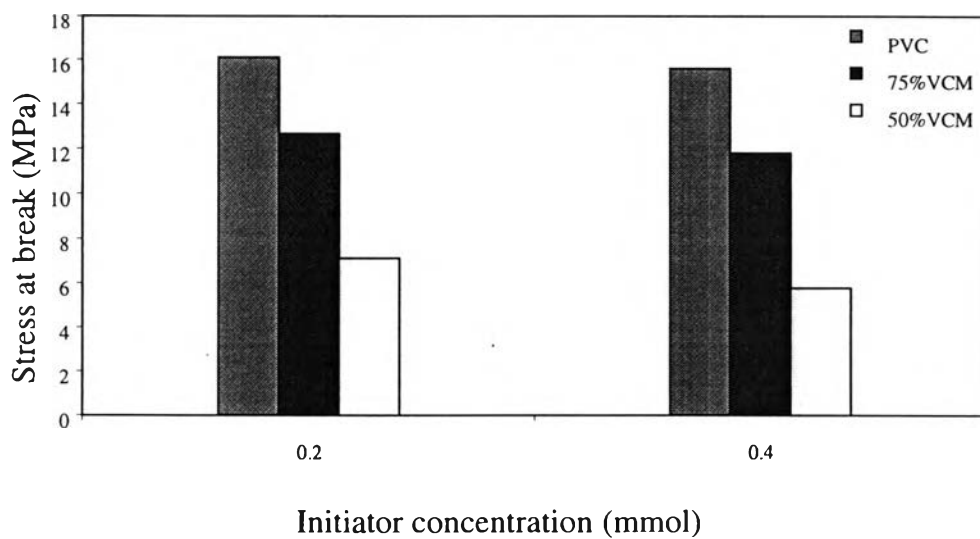


Figure 5.2 Relationships between initiator concentrations and stress at break of PVC and copolymers at 50°C polymerization temperature.

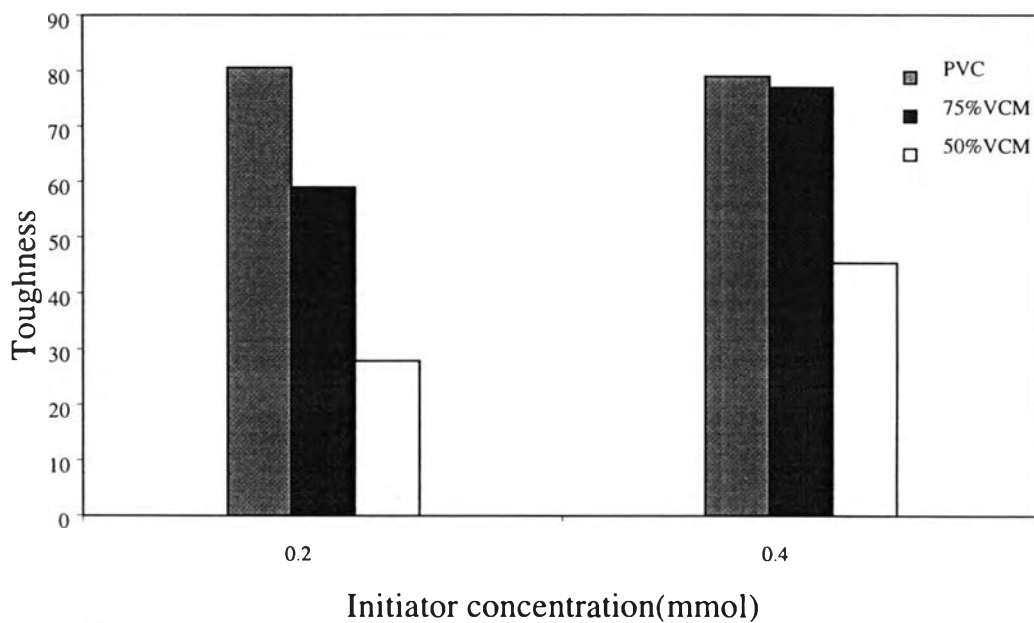


Figure 5.3 Relationships between initiator concentration and toughness of PVC and copolymers at 30°C polymerization temperature.

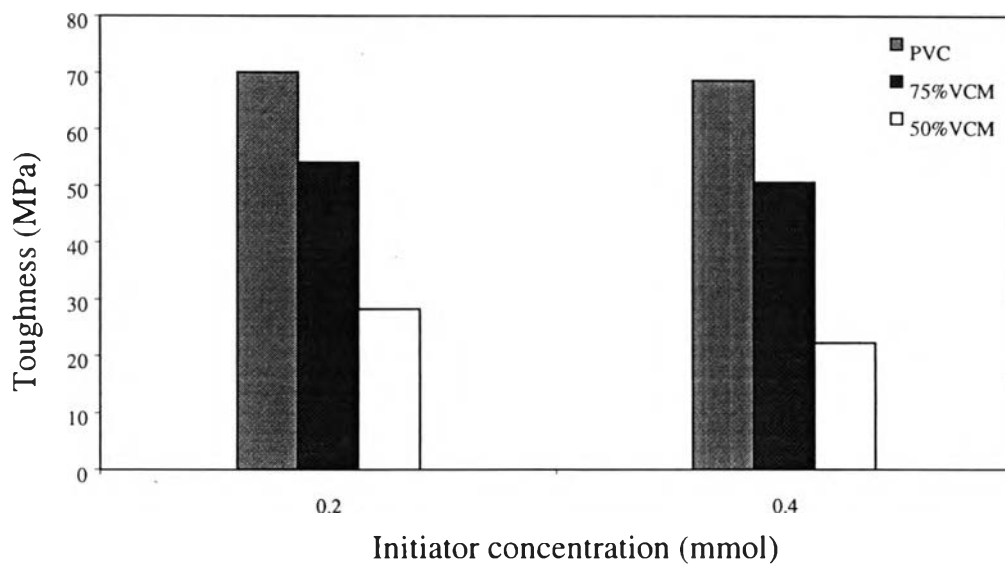


Figure 5.4 Relationships between initiator concentration and toughness of PVC and copolymers at 50°C polymerization temperature.

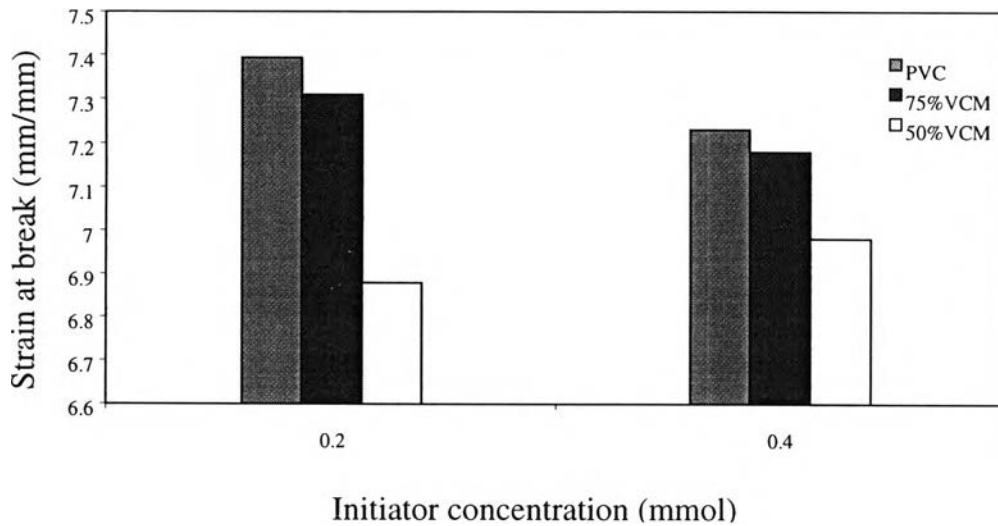


Figure 5.5 Relationships between initiator concentrations and strain at break of PVC and copolymers at 30°C polymerization temperature

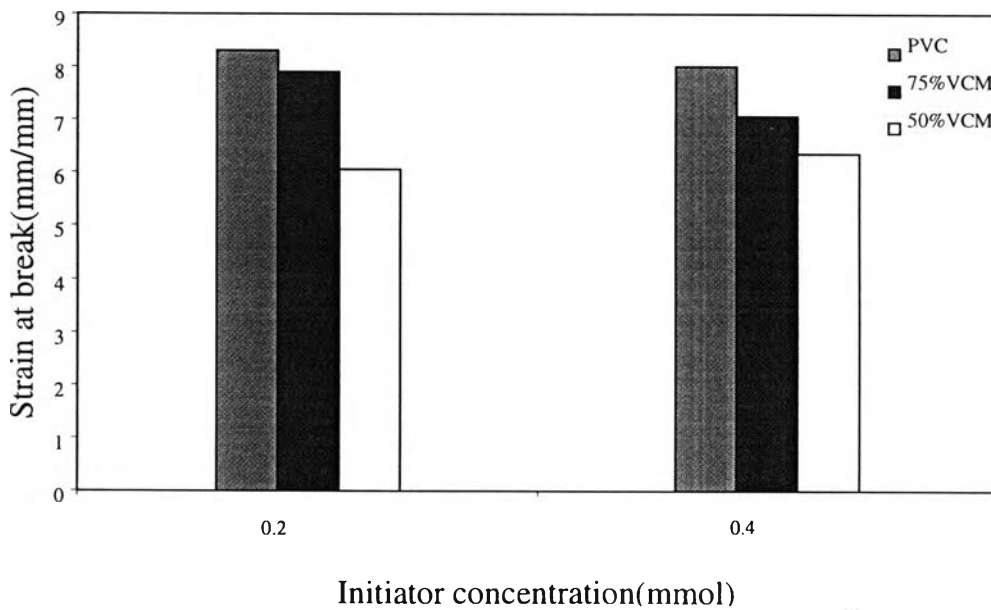


Figure 5.6 Relationships between initiator concentration and strain at break of PVC and copolymers at 50°C polymerization temperature.