

## Ultradrawing Gel Films of Blends of Ultrahigh-Molecular-Weight Polyethylene and Low-Molecular-Weight Polyethylenes with Varying Short-Chain Branched Lengths

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**ABSTRACT:** Ultradrawing of a series of films produced by gelation/crystallization from dilute decalin solutions of ultrahigh-molecular-weight polyethylene (UHMWPE) and low-molecular-weight polyethylenes (LMWPEs) with about the same molecular weight but varying short-chain branched lengths was reported. The achievable maximum draw ratios of gel films prepared from these solutions were found to depend significantly upon the concentrations of the solutions. It is worth noting that addition of less than about 5 wt% of LMWPE in UHMWPE/LMWPE blend gel films significantly improve their critical draw ratios ( $\lambda_c$ ) than that of gel films prepared from pure UHMWPE solution, and this improvement in  $\lambda_c$  is further enhanced with decreasing short-chain branched lengths of LMWPEs. These interesting phenomena were investigated in terms of the reduced viscosities of these solutions, tie molecule densities, morphology, melting, tensile and birefringence of these undrawn and/or drawn films.

**KEY WORDS** Ultrahigh-Molecular-Weight Polyethylene / Low-Molecular-Weight Polyethylenes / Critical Draw Ratio / Short-Chain Branches /

There has been good progress in new processing methods for obtaining high performance fibers of ultrahigh-molecular-weight polyethylene (UHMWPE).<sup>1–11</sup> Among these processing method, the gel spinning/casting method<sup>2,3</sup> has attracted many attentions since its invention in 1970s. This is probably due to its availability in production of high strength/modulus fibers commercially. The method by ultradrawing the gel specimens prepared by quenching solutions of UHMWPE is referred to as the gel deformation methods. The drawability of these gel specimens were found to depend principally on the concentration of the solution from which the gel was made.<sup>12,13</sup> The achievable draw ratios of the gel films reached a maximum, when they were prepared near their critical concentrations. However, the achievable drawability reduced significantly as the gel films were prepared from the solution of concentrations deviated from their critical values, at which the numbers of entanglements in the coherent network structure of the gel films are too many or too few to yield the maximum extension of UHMWPE during the gel deformation process.

Recently, ultradrawing gel films of UHMWPE and low-molecular-weight polyethylene (LMWPE) blend has been used to prepare high modulus fibers.<sup>14,15</sup> It has been reported that the modulus of the fiber prepared from ultradrawn gel film of 50/50 UHMWPE/LMWPE blend can reach as high as 80 GPa. In our recent study,<sup>16</sup> the maximum achievable draw ratios obtained for gel films prepared near their critical concentrations decrease significantly as they are associated with a lower weight ratio of UHMWPE to short-chain branched polyethylene (SBPE), wherein SBPE is a LMWPE. However, the maximum achievable draw ratios of the gel films with less than 2:98 weight ratio of SBPE to UHMWPE are even higher than that of gel film prepared from pure

UHMWPE solution. Such fibers and ultradrawn gel films of UHMWPE/LMWPE blend are very important commercially, because the production rate of high modulus fibers prepared from UHMWPE gels is far below that commercially required and the drawability of gel films prepared from pure UHMWPE solution can be lower than those of gel films prepared from UHMWPE/LMWPE blends because the enormous entanglements of UHMWPE gel films may prohibit the drawability of the gel films. However, very few investigations have ever been reported with regard to the preparation and drawing of the gel films of UHMWPE/LMWPE blends.

In this study, three different LMWPEs with about the same average length of main chain molecules but different branch lengths were added in UHMWPE solution to prepare and investigate the drawing behavior of the gel films of UHMWPE/LMWPE blends. The short-chain branched lengths of these LMWPEs were found to show significant effects on the drawing behavior, maximum achievable draw ratios and thermal properties of these gel films. Possible mechanisms accounting for these phenomena were discussed in this study.

### EXPERIMENTAL

#### *Materials and Preparation*

One UHMWPE resin and three LMWPEs with about the same molecular weight but different branch lengths were selected for this study. UHMWPE is associated with an weight average molecular weight ( $\bar{M}_w$ ) of  $4.5 \times 10^6$ , which will be referred to as resin U in the following discussion. Resin U was kindly supplied by Mr. Bruce Lu of Yung Chia Chemical Industries Corporation. On the other hand, the three LMWPEs will be referred to as resin L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>, respectively. Resin L<sub>1</sub> is a linear high density polyethylene with a weight average molecular weight of  $8.9 \times 10^4$ , which was also kindly supplied by Mr. Lu of Yung Chia Chemical

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Industries Corporation. Resins L<sub>2</sub> and L<sub>3</sub> are commercial SBPEs with approximately 18 ethyl and hexyl branches per thousand carbon atoms, respectively. The weight average molecular weight of resins L<sub>2</sub> and L<sub>3</sub> are  $9.2 \times 10^4$  and  $9.7 \times 10^4$ , respectively. Although  $\bar{M}_w$  increases slightly for LMWPE associated with longer branch length, this increase may in fact reflect the increase in length of short-chain branches rather than that of the main chain of LMWPE. The molecular weight distribution curve of these resins are very similar and  $\bar{M}_w/\bar{M}_n$  associated with resins L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> are 3.2, 3.4, and 3.6, respectively. Detailed characterization of the branched structure, molecular weight and molecular weight distribution of L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> resins was reported in our previous publications.<sup>17,18</sup> Mixtures of different weight ratios of UHMWPE to LMWPE were dissolved in decalin at 135°C for 90 min. About 0.1 wt% of di-*t*-butyl-*p*-cresol was added in the decalin solution as an antioxidant. The compositions of the gel solutions prepared above were summarized in Tables I—III. The hot homogenized solution was poured into an alumina tray and cooled in an oven to form a gel film at 35°C. The decalin was then evaporated from the gel in the oven. The dried gel was immersed in ethanol to remove antioxidant and residual trace of decalin. The prepared gel film had a thickness of about 250 μm. No gel film can be obtained from pure LMWPE solutions, which is possibly due to their low molecular weights and lack of entanglements in the LMWPE solutions. The percentage of crystallinities of the fragments of the dry gels of pure L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> prepared at concentrations ranging from 5 to 10 g/100 ml are about 80%, 57%, and 47%, respectively.

## CHARACTERIZATION

### *Viscosity Measurements and Thermal Analysis*

The viscosities of polymer solutions were determined at 135°C by a Brookfield viscometer model LVDV-II<sup>+</sup>. The thermal behavior of all samples was performed on a Dupont differential scanning calorimeter (DSC) model 2000. All scans were carried out at a heating rate of 10°C min<sup>-1</sup> under flowing nitrogen at a flow rate of 25 ml min<sup>-1</sup>. Samples weighing 10 mg and 0.5 mg were placed in the standard aluminum sample pans for determination of the degree of crystallinity and melting temperature, respectively. Degrees of crystallinity of all samples were estimated using baselines drawn from 40 to 170°C and a perfect heat fusion of 293 J g<sup>-1</sup>.<sup>19</sup>

### *Morphology and Birefringence of the Gel Films*

The morphology of the drawn and undrawn gel films was analyzed using a JEOL JSM-5200 scanning electron microscope (SEM) and a Leica TP-91 optical microscope. Prior to SEM examination, all specimens were coated by a vacuum-evaporated layer of gold for about 30 s at 10 mA. Birefringence of the drawn and undrawn gel films was measured by using a polarizing micro-spectrometer model TFM-120 AFT.

### *Tie Molecule Density*

Tie molecules have been characterized by using such techniques as transmission electron microscopy,<sup>20–27</sup>

neutron scattering<sup>28</sup> and nuclear magnetic resonance,<sup>29</sup> and by measurement of the brittle tensile strength.<sup>30</sup> However, due to the small dimensions and complexity of the intercrystalline links, these techniques (excluding the last one) do not appear to be suitable for ready analysis of a relatively large number of bulk samples. In this study, tie molecule density of the gel film was not measured directly, but was evaluated from brittle tensile strength measurements. As mentioned previously, no gel film can be obtained from pure LMWPE (*i.e.*, L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>) solutions. The quantitative ranking of tie molecule density of LMWPEs of different branched lengths was evaluated from the injection-molded LMWPE specimens. We are not suggesting that the brittle fracture stress approach provides a precise measurement of the tie molecule density, but rather qualitative information which will allow a comparison between various samples. The brittle tensile strength ( $\sigma_f$ ) of gel film and injection-molded specimens was also determined on a Tensilon testing machine model RTA-1T at a temperature of about -110°C and a crosshead speed of 50 cm min<sup>-1</sup>. A minimum of four samples of each specimen type were tested and averaged. Brown and Ward<sup>30</sup> proposed a model which allows one to estimate the fraction of the interlamellar area covered by tie molecules ( $f_T$ ):

$$f_T = \frac{C\sigma_f - \beta E_{iso}}{\beta(E_T - E_{iso})}$$

where  $C$  represents the stress concentration,  $\beta$  is a constant of proportionality,  $E_{iso}$  the Young's modulus for van der Waals' bonds, and  $E_T$  the Young's modulus of the tie chains. For purposes of comparison we use  $C=20$ ,  $\beta=0.1$ ,  $E_{iso}=8$  GPa, and  $E_T=300$  GPa as proposed by Brown and Ward for polyethylene. The enormous numbers of inter and intramolecular entanglements of polymers are generally believed to be mostly preserved after crystallization, and they are most likely present between crystal lamellae and acts as tie molecules after crystallization. The evaluated tie molecule densities of the gel films and melt crystallized LMWPEs are, therefore, used to relate to the level of entanglements present in the gel films or melt-crystallized LMWPEs before and after crystallization.

### *Drawing and Tensile Properties of the Gel Films*

The drawing and tensile properties of the undrawn and drawn gel films was studied using a Tensilon testing machine model RTA-1T equipped with an environmental chamber. The strip specimens with a dimension of 30 mm in length and 10 mm in width were cut from the dry gel films. The strip specimens were clamped in a stretching device and then stretched at a crosshead speed of 20 mm min<sup>-1</sup> and a constant temperature of 95°C. The draw ratio of each specimen was determined as the ratio of the marked displacement after and before drawing. The marked displacement before drawing was 5 mm. Preliminary experiments showed that the optimum drawing temperatures for these dry gel films were approximate ranging from 95 to 115°C, and the gel films became too soft to draw and can only reach a relatively low draw ratio at temperatures greater than 120°C. At 135°C, the maximum draw ratios of the dry gel film of

**Table I.** The weight ratio of U to LMWPE (WR), concentration, critical concentration ( $C_c$ ), draw ratio, and melting temperatures of each gel film of UL<sub>1</sub> series

Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$	Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$
		g/100 ml	g/100 ml		°C			g/100 ml	g/100 ml		°C
U <sub>0.6</sub>	100/0	0.6	0.7	216	140	UL <sub>1-C-0.7</sub>	90/10	0.7	0.85	195	137
U <sub>0.7</sub>		0.7		240	140	UL <sub>1-C-0.8</sub>		0.8		204	138
U <sub>0.8</sub>		0.8		224	140	UL <sub>1-C-0.9</sub>		0.9		229	137
U <sub>0.9</sub>		0.9		221	140	UL <sub>1-C-1.0</sub>		1.0		213	137
U <sub>1.0</sub>		1.0		200	140	UL <sub>1-C-1.1</sub>		1.1		169	136
UL <sub>1-A-0.6</sub>	98/2	0.6	0.76	277	139	UL <sub>1-D-0.9</sub>	80/20	0.9	1.13	145	137
UL <sub>1-A-0.7</sub>		0.7		360	138	UL <sub>1-D-1.0</sub>		1.0		184	136
UL <sub>1-A-0.8</sub>		0.8		288	138	UL <sub>1-D-1.1</sub>		1.1		200	137
UL <sub>1-A-0.9</sub>		0.9		268	138	UL <sub>1-D-1.2</sub>		1.2		175	137
UL <sub>1-A-1.0</sub>		1.0		233	138	UL <sub>1-D-1.3</sub>		1.3		140	137
UL <sub>1-B-0.6</sub>	95/5	0.6	0.84	210	138	UL <sub>1-E-1.0</sub>	70/30	1.0	1.28	115	137
UL <sub>1-B-0.7</sub>		0.7		226	138	UL <sub>1-E-1.1</sub>		1.1		121	136
UL <sub>1-B-0.8</sub>		0.8		295	137	UL <sub>1-E-1.2</sub>		1.2		144	137
UL <sub>1-B-0.9</sub>		0.9		285	138	UL <sub>1-E-1.3</sub>		1.3		123	136
UL <sub>1-B-1.0</sub>		1.0		240	137	UL <sub>1-E-1.4</sub>		1.4		105	137

**Table II.** The weight ratio of U to LMWPE (WR), concentration, critical concentration ( $C_c$ ), draw ratio, and melting temperatures of each gel film of UL<sub>2</sub> series

Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$	Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$
		g/100 ml	g/100 ml		°C			g/100 ml	g/100 ml		°C
U <sub>0.6</sub>	100/0	0.6	0.7	216	140	UL <sub>2-C-0.7</sub>	90/10	0.7	0.86	180	138
U <sub>0.7</sub>		0.7		240	140	UL <sub>2-C-0.8</sub>		0.8		195	137
U <sub>0.8</sub>		0.8		224	140	UL <sub>2-C-0.9</sub>		0.9		218	137
U <sub>0.9</sub>		0.9		221	140	UL <sub>2-C-1.0</sub>		1.0		202	138
U <sub>1.0</sub>		1.0		200	140	UL <sub>2-C-1.1</sub>		1.1		165	137
UL <sub>2-A-0.6</sub>	98/2	0.6	0.76	241	137	UL <sub>2-D-0.9</sub>	80/20	0.9	1.13	135	136
UL <sub>2-A-0.7</sub>		0.7		295	138	UL <sub>2-D-1.0</sub>		1.0		165	137
UL <sub>2-A-0.8</sub>		0.8		250	138	UL <sub>2-D-1.1</sub>		1.1		184	137
UL <sub>2-A-0.9</sub>		0.9		255	138	UL <sub>2-D-1.2</sub>		1.2		162	136
UL <sub>2-A-1.0</sub>		1.0		220	138	UL <sub>2-D-1.3</sub>		1.3		135	136
UL <sub>2-B-0.7</sub>	95/5	0.7	0.84	200	138	UL <sub>2-E-1.0</sub>	70/30	1.0	1.29	105	136
UL <sub>2-B-0.8</sub>		0.8		215	138	UL <sub>2-E-1.1</sub>		1.1		112	136
UL <sub>2-B-0.9</sub>		0.9		256	137	UL <sub>2-E-1.2</sub>		1.2		140	136
UL <sub>2-B-1.0</sub>		1.0		234	138	UL <sub>2-E-1.3</sub>		1.3		115	136
UL <sub>2-B-1.1</sub>		1.0		217	138	UL <sub>2-E-1.4</sub>		1.4		95	137

**Table III.** The weight ratio of U to LMWPE (WR), concentration, critical concentration ( $C_c$ ), draw ratio, and melting temperatures of each gel film of UL<sub>3</sub> series

Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$	Sample	WR	Concentration	$C_c$	Draw ratio	$T_{m1}$
		g/100 ml	g/100 ml		°C			g/100 ml	g/100 ml		°C
U <sub>0.6</sub>	100/0	0.6	0.7	216	140	UL <sub>3-C-0.6</sub>	90/10	0.6	0.85	177	138
U <sub>0.7</sub>		0.7		240	140	UL <sub>3-C-0.7</sub>		0.7		188	138
U <sub>0.8</sub>		0.8		224	140	UL <sub>3-C-0.8</sub>		0.8		190	138
U <sub>0.9</sub>		0.9		221	140	UL <sub>3-C-0.9</sub>		0.9		150	137
U <sub>1.0</sub>		1.0		200	140	UL <sub>3-C-1.0</sub>		1.0		147	137
UL <sub>3-A-0.6</sub>	98/2	0.6	0.76	229	138	UL <sub>3-D-0.8</sub>	80/20	0.8	1.12	100	137
UL <sub>3-A-0.7</sub>		0.7		264	138	UL <sub>3-D-0.9</sub>		0.9		101	136
UL <sub>3-A-0.8</sub>		0.8		259	138	UL <sub>3-D-1.0</sub>		1.0		110	136
UL <sub>3-A-0.9</sub>		0.9		226	138	UL <sub>3-D-1.1</sub>		1.1		152	137
UL <sub>3-A-1.0</sub>		1.0		221	138	UL <sub>3-D-1.2</sub>		1.2		119	136
UL <sub>3-B-0.7</sub>	95/5	0.7	0.83	187	138	UL <sub>3-E-1.0</sub>	70/30	1.0	1.30	58	136
UL <sub>3-B-0.8</sub>		0.8		223	137	UL <sub>3-E-1.1</sub>		1.1		62	135
UL <sub>3-B-0.9</sub>		0.9		167	138	UL <sub>3-E-1.2</sub>		1.2		77	136
UL <sub>3-B-1.0</sub>		1.0		159	138	UL <sub>3-E-1.3</sub>		1.3		84	136
UL <sub>3-B-1.1</sub>		1.1		154	138	UL <sub>3-E-1.4</sub>		1.4		76	136

pure UHMWPE prepared at concentrations ranging from 0.6 to 1.0 g/100 ml were less than 60 at a drawing rate of 20 mm min<sup>-1</sup>. The drawing temperature was then selected as 95°C.

## RESULTS AND DISCUSSION

### Evaluation of Tie Molecule Density

The evaluated tie molecule densities ( $f_{TS}$ ) of the gel films and melt crystallized LMWPEs were summarized in Table IV. It is worth noting that  $f_{TS}$  of the gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series decreased significantly with increasing composition of LMWPEs present in gel films of UHMWPE/LMWPE blends. As mentioned in the experimental section, the melt crystallized L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> were utilized to evaluate the tie molecule densities of LMWPEs because no gel film can be prepared from pure LMWPE solutions. As shown in Table IV, the evaluated tie molecule densities of the melt crystallized LMWPEs are significantly larger than those of gel films of UHMWPE/LMWPE. This is possibly due to the fact that the gel films were prepared from highly dilute solutions of UHMWPE/LMWPE, which dramatically reduces their inter and intramolecular entanglements than those of melt crystallized samples. In addition, it is worth noting that the tie molecule densities increase significantly with increasing branch lengths of these melt crystallized LMWPEs. However, as described in experimental section, degrees of crystallinity ( $W_c$ ) of gel fragments of LMWPEs prepared at concentrations ranging from 5 to 10 g/100 ml decrease approximately from 80% to 57% and 47% as the branch lengths of LMWPEs increased from 0 to 2 and 6 carbon-atom lengths. These results are possibly due to the increase in lengths of short-chain branches of LMWPEs, which can significantly prohibit the incorporation of polymer chains into crystal lattices of LMWPEs and retain more inter and intramolecular entanglements of LMWPE molecules during crystallization, and, hence, results in a lower  $W_c$  and higher  $f_T$ . Similar to those found in melt crystallized LMWPEs,  $f_{TS}$  of gel films of UHMWPE/LMWPE also increase significantly with increasing branch lengths of LMWPEs, when the gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series were associated with large and fixed compositions of LMWPEs (see UL<sub>X-D-1.0</sub> and UL<sub>X-E-1.0</sub> series). However, this increase in  $f_T$  with increasing branched lengths of LMWPEs was not found in gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series associated with small and fixed compositions of LMWPEs (see Table IV). This is possible due to the lackage of sensitivity of brittle fracture stress approach in distinguishing the small difference in  $f_T$  within these sample series. Presumably, this increase in  $f_T$  with increasing branched lengths of LMWPEs is also believed to occur in gel films associated with small and fixed compositions of LMWPEs in UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series.

### Critical Concentrations of UHMWPE/LMWPE Solutions

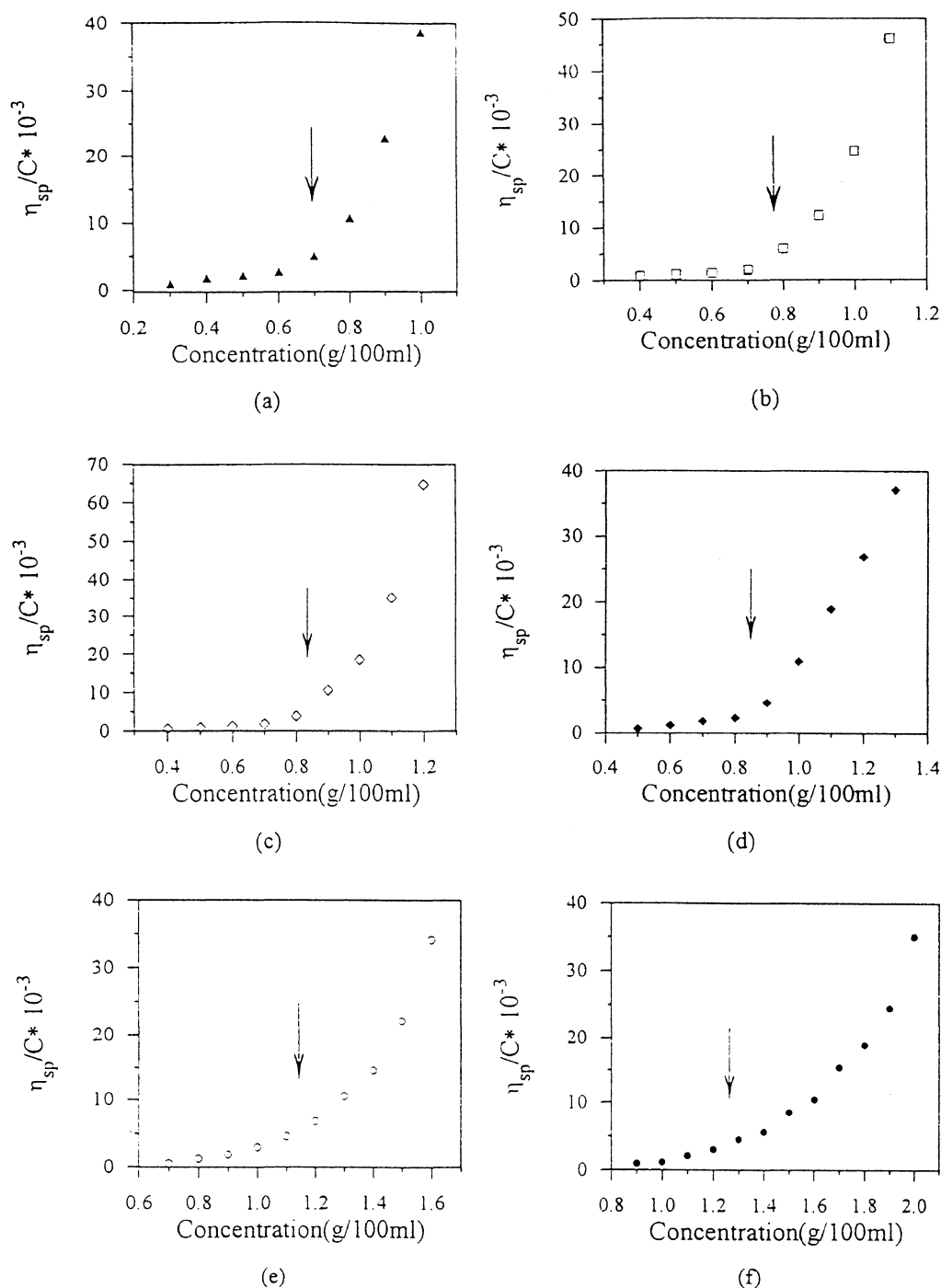
The typical plot of reduced viscosities ( $\eta_{sp}/C$ ) against the concentrations of UHMWPE/LMWPE and UHMWPE solutions are shown in Figure 1. The reduced viscosities of these solutions increased dramatically as

**Table IV.** Tie molecule densities ( $f_{TS}$ ) of gel films and melt crystallized samples

Sample	Tie molecule density ( $f_T$ )/%
U <sub>1.0</sub>	0.135
UL <sub>1-A-1.0</sub>	0.135
UL <sub>1-B-1.0</sub>	0.126
UL <sub>1-C-1.0</sub>	0.112
UL <sub>1-D-1.0</sub>	0.095
UL <sub>1-E-1.0</sub>	0.078
UL <sub>2-A-1.0</sub>	0.135
UL <sub>2-B-1.0</sub>	0.127
UL <sub>2-C-1.0</sub>	0.116
UL <sub>2-D-1.0</sub>	0.102
UL <sub>2-E-1.0</sub>	0.089
UL <sub>3-A-1.0</sub>	0.135
UL <sub>3-B-1.0</sub>	0.129
UL <sub>3-C-1.0</sub>	0.119
UL <sub>3-D-1.0</sub>	0.114
UL <sub>3-E-1.0</sub>	0.105
Melt crystallized	
L <sub>1</sub>	1.400
L <sub>2</sub>	2.800
L <sub>3</sub>	4.200

the concentrations of solutions reached the "critical" value, whereas only slight increase in  $\eta_{sp}/C$  were found as the concentrations of solutions increased up to the critical value. Similar concentration dependence of the reduced viscosity of pure UHMWPE solution was found by several authors.<sup>12,13</sup> This critical value of concentration shifted to a higher value with decreasing weight ratio of UHMWPE to LMWPE (*i.e.*, L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>) associated with each UHMWPE/LMWPE solution, which was referred to as the "critical concentration ( $C_c$ )" of each UHMWPE/LMWPE or UHMWPE solution in the literature.<sup>12,13,16</sup>

On the other hand, the critical concentrations remained at approximately the same value for UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> solution series associated with a fixed weight ratio of UHMWPE to LMWPE, although the branched lengths of L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> are different (Tables I—III and Figure 1). The critical concentration is generally interpreted<sup>13</sup> as a concentration at which the coherent network of UHMWPE molecules was formed. As described in previous section, the increase in short-chain branched lengths of LMWPEs may enhance the number of entanglements between LMWPE molecules in solutions and, hence, the evaluated tie molecule density was found to increase within the solid phase of LMWPE. However, the entanglements within LMWPE and/or between LMWPE and UHMWPE molecules in gel solutions of UHMWPE/LMWPE are weak before solidification as compared to those between UHMWPE molecules, which may easily be disentangled and contribute little during the viscosity measurements of UHMWPE/LMWPE solutions. Based on these premises, it is reasonable to suggest that the difference in branch lengths of these LMWPEs can not significantly affect the  $\eta_{sp}/C$  of UHMWPE/LMWPE solutions. As a consequence, about the same value of  $C_c$  was found for UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> solution



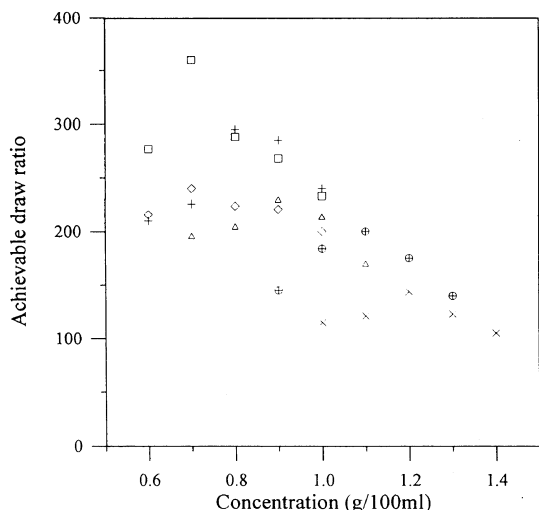
**Figure 1.** Reduced viscosity ( $\eta_{sp}/C$ ) of the solution of sample (a) U, (b) UL<sub>1-A</sub>, (c) UL<sub>1-B</sub>, (d) UL<sub>1-C</sub>, (e) UL<sub>1-D</sub>, and (f) UL<sub>1-E</sub> series. (Arrow indicates the critical concentration.)

series when they were associated with a fixed weight ratio of UHMWPE to LMWPE. However, the number of inter and intramolecular entanglements of UHMWPE are significantly reduced with the addition of LMWPE in solutions of a fixed concentration of UHMWPE/LMWPE because the average lengths of the main chain of  $L_1$ ,  $L_2$ , and  $L_3$  are approximately the same, and are significantly shorter than that of UHMWPE. This idea was supported by the evidence that  $f_{TS}$  reduced significantly with increasing composition of LMWPE present in gel films of UHMWPE/LMWPE blends (see Table IV). In order to maintain the coherent network of UHMWPE molecules in UHMWPE/LMWPE solution, the amount of UHMWPE present in solution must in-

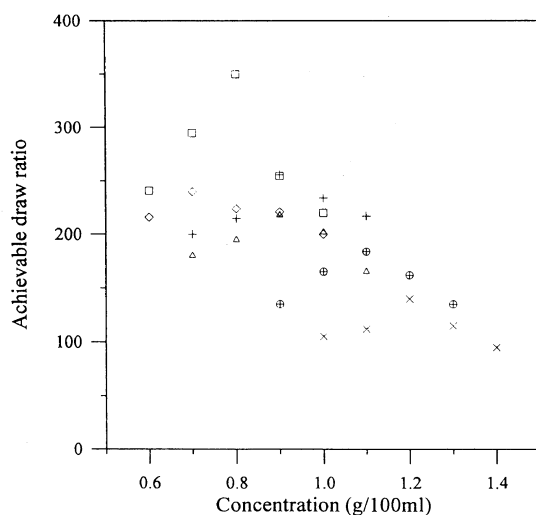
crease to an appropriate value. The value of  $C_c$  was, therefore, found to increase to a higher values as the weight ratio of UHMWPE to LMWPE in UHMWPE/LMWPE solutions decreased.

#### *Achievable Draw Ratios of UHMWPE/LMWPE Gel Films*

The achievable draw ratios of the gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series were summarized in Figures 2–4 and Tables I–III. Similar to those found in our previous investigation,<sup>16</sup> the achievable draw ratios of the gel films prepared from each weight ratio of UHMWPE to LMWPE (WR) approached a maximum value, when they were prepared at concentrations close to their critical

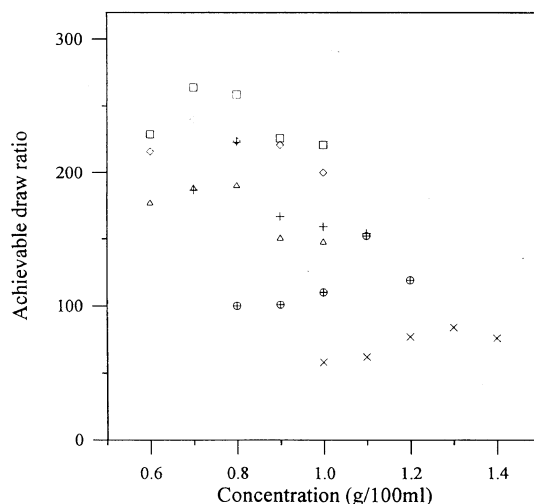


**Figure 2.** The achievable draw ratios of gel films of samples (◇) U, (□) UL<sub>1-A</sub>, (+) UL<sub>1-B</sub>, (△) UL<sub>1-C</sub>, (⊕) UL<sub>1-D</sub>, and (×) UL<sub>1-E</sub> series prepared at varying concentrations.

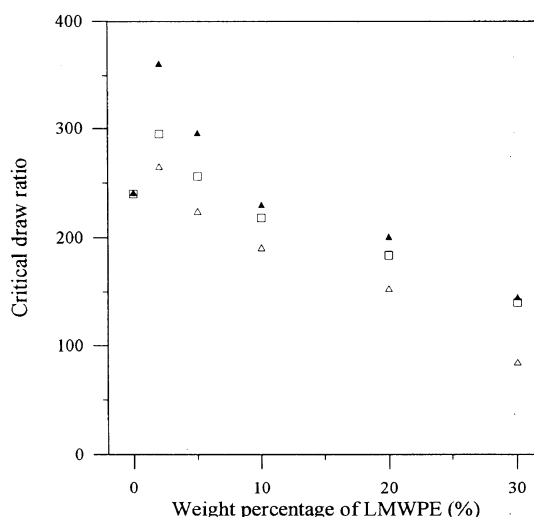


**Figure 3.** The achievable draw ratios of gel films of samples (◇) U, (□) UL<sub>2-A</sub>, (+) UL<sub>2-B</sub>, (△) UL<sub>2-C</sub>, (⊕) UL<sub>2-D</sub>, and (×) UL<sub>2-E</sub> series prepared at varying concentrations.

concentrations (Figures 2—4). These achievable draw ratios obtained for samples prepared near their critical concentrations will be referred to as the critical draw ratio ( $\lambda_c$ ) in the following discussion. Figure 5 shows the critical draw ratios as a function of weight percentage of LMWPE present in gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series. The critical draw ratios of the gel films containing small percentage of LMWPE in UHMWPE are significantly higher than that of the gel film of pure UHMWPE. For instance, the critical draw ratios of UL<sub>1</sub> gel films with less than about 5% LMWPE are at least 20% higher than that of gel films of pure UHMWPE. In fact, the maximum critical draw ratio of gel films of UL<sub>1</sub> series (*i.e.*, samples UL<sub>1-A</sub> series) is about 50% higher than that of the gel film prepared from pure UHMWPE solution. It is further interesting to note that the maximum  $\lambda_c$  of the gel films of UL<sub>1</sub> series is slightly higher but significantly higher than those of UL<sub>2</sub> and UL<sub>3</sub> series, respectively (Figure 5 and Tables I—III). As mentioned previously, the average lengths of the main chains of L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> are about the same, wherein

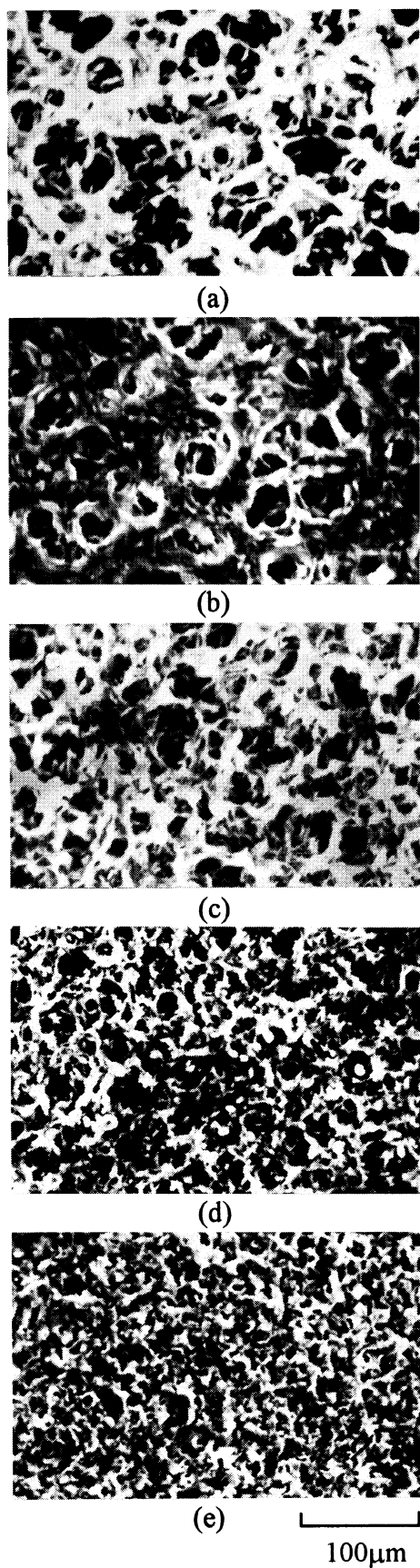


**Figure 4.** The achievable draw ratios of gel films of samples (◇) U, (□) UL<sub>3-A</sub>, (+) UL<sub>3-B</sub>, (△) UL<sub>3-C</sub>, (⊕) UL<sub>3-D</sub>, and (×) UL<sub>3-E</sub> series prepared at varying concentrations.

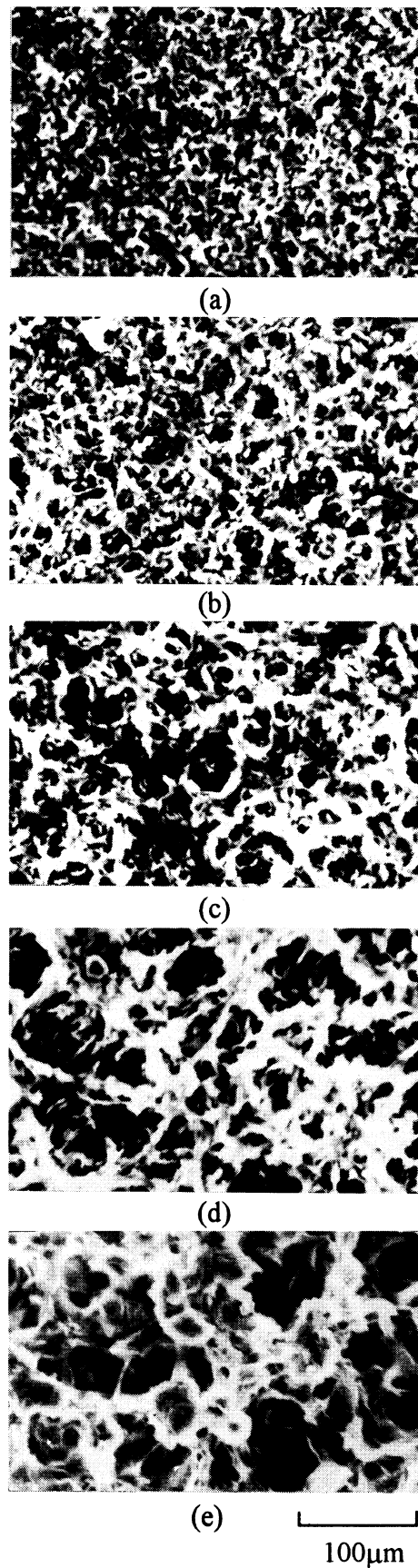


**Figure 5.** Plots of critical draw ratios *versus* the weight percentage of LMWPE in the gel films of (▲) UL<sub>1</sub>, (□) UL<sub>2</sub>, and (△) UL<sub>3</sub> series.

L<sub>1</sub> is a linear LMWPE and the length of short chain branches of L<sub>3</sub> is longer than that of L<sub>2</sub>. These results suggest that the presence of optimum amounts of LMWPE in gel films of UHMWPE/LMWPE blends can significantly improve their critical draw ratios, and this improvement in  $\lambda_c$  is further enhanced with decreasing branch lengths of the short chain branches of LMWPEs. It is not completely clear what accounts for these interesting behaviors. One possible explanation for these drawing behaviors is that presence of LMWPEs in UHMWPE gel films may cause some defects in the lamellar crystals, crystal boundaries, or amorphous regions of UHMWPE. On the other hand, the presence of LMWPEs in gel films of UHMWPE/LMWPE can also significantly reduce the number of inter and intramolecular entanglements of UHMWPE in gel films of UHMWPE/LMWPE. These crystal defects and reduced number of inter and intramolecular entanglements of UHMWPE increase with increasing composition of LMWPEs present in gel films of UHMWPE/LMWPE, which can cause stress concentration on the significantly reduced tie molecules, and early break-



**Figure 6.** Scanning electron micrographs of gel films of samples (a)  $UL_{1-A-0.6}$ , (b)  $UL_{1-A-0.7}$ , (c)  $UL_{1-A-0.8}$ , (d)  $UL_{1-A-0.9}$ , and (e)  $UL_{1-A-1.0}$ .



**Figure 7.** Scanning electron micrographs of gel films of samples (a)  $UL_{1-A-1.0}$ , (b)  $UL_{1-B-1.0}$ , (c)  $UL_{1-C-1.0}$ , (d)  $UL_{1-D-1.0}$ , and (e)  $UL_{1-E-1.0}$ .

age of UHMWPE molecules in crystal boundaries or the amorphous regions of UHMWPE during the drawing process of these gel films. A significant reduction of  $\lambda_c$  with increasing amounts of LMWPEs added was then observed. However, it is also well recognized that slightly decrease in the enormous number of inter and intramolecular entanglements of UHMWPE can help disentangling UHMWPE molecules and pulling them out of lamellar crystals during the drawing process if the amounts of LMWPEs present in gel films of UHMWPE/LMWPE are less than a critical value, at which the "stress concentration" effect caused by the "crystal defects" and significantly reduced tie molecules is overcome by the "beneficial drawing" effect mentioned above. In addition, the evaluated number of tie molecules within LMWPEs was found to decrease significantly with decreasing lengths of the short chain branches. Presumably, this significantly reduced entanglements within LMWPEs with shorter branch lengths is believed to further enhance the disentanglement of UHMWPE molecules and pulling them out of lamellar crystals during the drawing process of gel films. It is, therefore, addition of a small but optimum amount of LMWPE in gel films of UHMWPE/LMWPE blends can significantly improve their  $\lambda_c$  better than that of gel film prepared from pure UHMWPE gel solution, and this improvement in  $\lambda_c$  is further enhanced with decreasing lengths of short chain branches of LMWPEs.

#### Morphology of the Undrawn and Drawn Gel Films

Figures 6 and 7 show the typical morphology of the dry gel films of UL<sub>1</sub> series. As shown in these SEM micrographs, porous structure was found on the surface of these undrawn gel films. Similar porous structures were also found by other investigators.<sup>31,32</sup> It is interesting to note that the porous structures appeared only on the surfaces of the gel films and became more densely distributed as they were prepared from a higher concentration of UL<sub>1</sub> solution series, respectively (Figure 6). Similar behavior was also found on dry gel films of UL<sub>2</sub> and UL<sub>3</sub> series. On the other hand, at a fixed concentration of UHMWPE/LMWPE, the porous structures became more sparsely distributed as the amounts of L<sub>1</sub>, L<sub>2</sub>, or L<sub>3</sub> present in the gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series increased, respectively (Figure 7). It is not completely clear what are the underlying mechanisms accounting for the formation of these porous structures. However, it seems reasonable to suggest that these porous structures are correlated to the coherent network structure of UHMWPE and the volarization process of the solvent during the preparation of gel films. As mentioned previously, the numbers of entanglements within coherent network structures of the gel solutions reduce significantly with increasing amounts of LMWPEs present in gel films. In contrast, the numbers of entanglements present in the coherent network structures of gel solutions increase significantly with increasing concentrations of the gel solutions. As a consequence, the porosity became significantly larger and sparsely distributed as the amounts of LMWPEs present in gel films and the concentrations of the gel solutions increased and decreased, respectively.

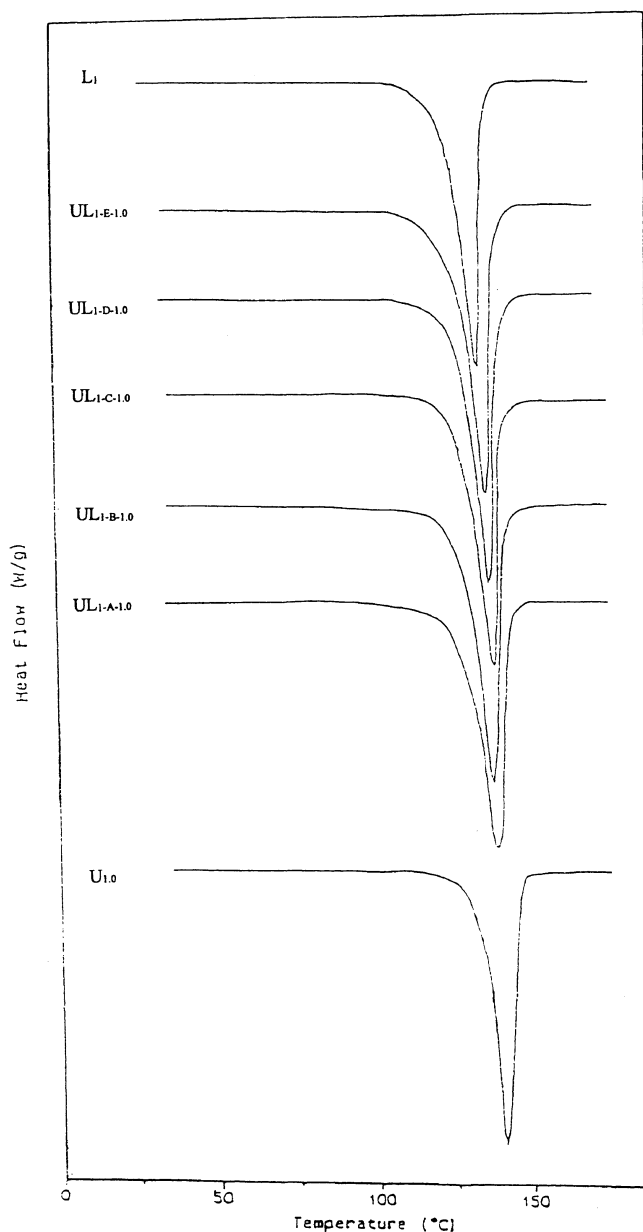
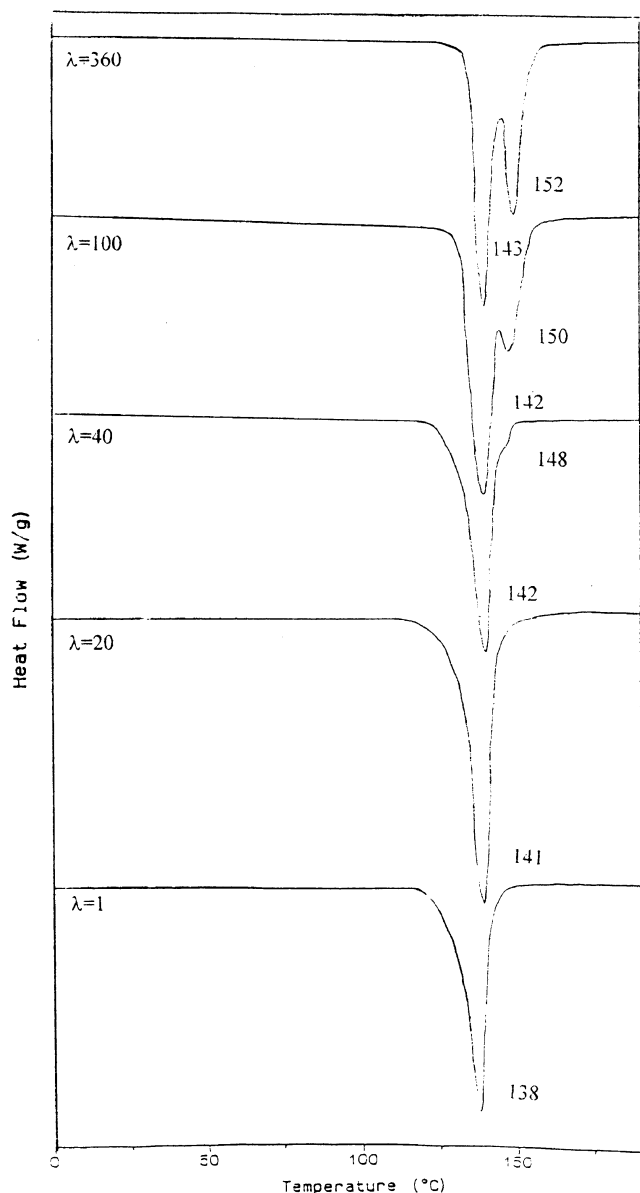


Figure 8. DSC thermograms of samples of pure L<sub>1</sub> and UL<sub>1</sub> series.

#### Thermal Analysis

The typical DSC thermograms of the gel films of pure UHMWPE and UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series is shown in Figure 8. All these thermograms exhibited a main melting peak originated from the melting endotherm of pure UHMWPE at about 140°C. This main melting temperature ( $T_m$ ) decreased significantly with the amounts of L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> present in the gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series, respectively. In addition to this main melting endotherm, another melting endotherms with onset temperatures of about 90°C became more distinguished as the amounts of short chain branched polyethylenes (*i.e.*, L<sub>2</sub> and L<sub>3</sub>) present in UL<sub>2</sub> and UL<sub>3</sub> gel films increased, respectively. The onset temperatures and melting temperatures of the lower melting endotherms of the gel films of UL<sub>2</sub> and UL<sub>3</sub> series are very close to those of films prepared from pure L<sub>2</sub> and L<sub>3</sub> solutions, respectively. These results suggested that these LMWPEs may cocrystallize with UHMWPE and make defects in the lamellar crystals of UHMWPE, which is

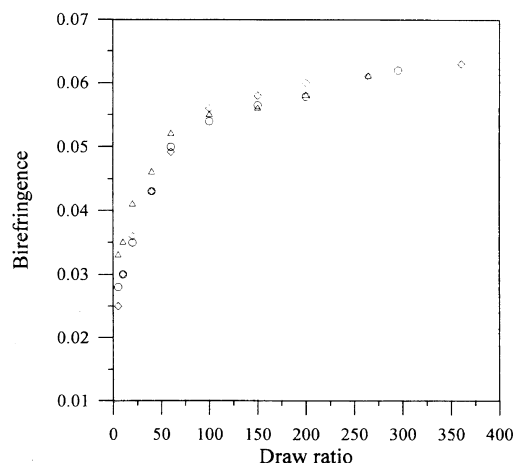




**Figure 9.** DSC thermograms of sample of UL<sub>1-A-0.7</sub> drawn at varying draw ratios.

evidenced by the decreasing main melting temperature with increasing amounts of L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> present in the gel films. However, part of these LMWPEs may tend to become phase separated with UHMWPE and crystallized independently in the amorphous regions of UHMWPE as the composition of LMWPE in gel films of UHMWPE/LMWPE increases.

Typical DSC thermograms of these gel films drawn at varying draw ratios are shown in Figure 9. The main melting temperature increases significantly with the draw ratio up to a temperature of around 143°C. A small shoulder at a temperature of about 148°C was found on the right of the main melting endotherm when these gel films were stretched to a draw ratio of about 40. In fact, this small shoulder continues to grow into another melting endotherm, and the temperature associated with this new melting peak increases up to about 152°C as the draw ratio reaches about 360. It is generally recognized that orientation of polymer chain and reduction of crystal defects during drawing can enhance



**Figure 10.** Birefringence of samples ( $\diamond$ ) UL<sub>1-A-0.7</sub>, ( $\circ$ ) UL<sub>2-A-0.7</sub>, and ( $\triangle$ ) UL<sub>3-A-0.7</sub> drawn at different draw ratios.

the perfection and melting temperature of the crystal. However, it is not completely clear why the “small shoulder” appeared at a draw ratio of around 40 and the melting temperatures associated with this new grown endotherm are even higher than the reported equilibrium melting temperature of polyethylene. Presumably, the appearance of double melting peaks is attributed to the constraint imposed on the highly drawn samples. This imposed samples may retain the oriented chain arrangement in the melt state for a short period of time. It is, therefore, the entropy of fusion of this oriented melt would obviously be smaller than that of melt associated with random coils, and, hence, an extraordinary high melting temperature is observed. Such a superheating phenomenon was also observed in ultra-drawing pure UHMWPE by other authors.<sup>33</sup>

#### *Birefringence and Tensile Properties of the Drawn Gel Films*

The birefringence of the drawn and undrawn gel films of typical samples UL<sub>1-A</sub>, UL<sub>2-A</sub>, and UL<sub>3-A</sub> series are shown in Figure 10. The value of birefringence increases consistently with the draw ratio, wherein the increasing rate of birefringence becomes slower as the draw ratio of the gel film is greater than about 40. Tensile strength and moduli of these drawn gel films were found to improved consistently with the draw ratios (Figures 11 and 12). As mentioned in previous section, the melting temperatures associated with the main and new grown melting endotherm of the drawn gel films also increase consistently with increasing draw ratios of the gel films, in which a “small shoulder” was found on the right of the main melting endotherm when these gel films were stretched to a draw ratio of about 40. However, it is not completely clear what accounts for these abrupt change in melting and birefringency properties as the draw ratio of the gel film reaches around 40. These results suggested that degree of orientation of UHMWPE molecules along the drawing direction increased consistently with the draw ratios of gel films, although they increased slightly slower as the draw ratios were greater than 40. The increase in degree of orientation of molecular chains along the drawing direction is suggested to be responsible for the improved tensile strength, modulus and melting temperature of the drawn gel films.

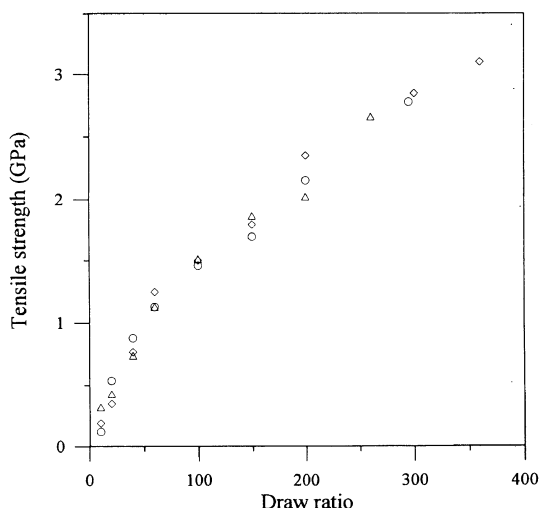


Figure 11. Tensile strengths of samples ( $\diamond$ ) UL<sub>1-A-0.7</sub>, ( $\circ$ ) UL<sub>2-A-0.7</sub>, and ( $\triangle$ ) UL<sub>3-A-0.7</sub> drawn at varying draw ratios.

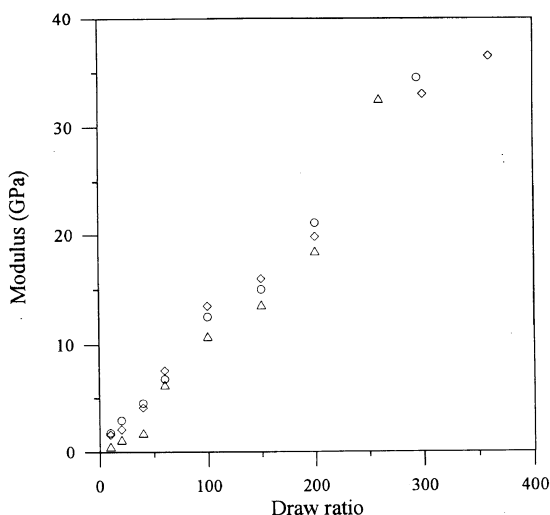


Figure 12. Moduli of samples ( $\diamond$ ) UL<sub>1-A-0.7</sub>, ( $\circ$ ) UL<sub>2-A-0.7</sub>, and ( $\triangle$ ) UL<sub>3-A-0.7</sub> drawn at varying draw ratios.

## CONCLUSIONS

The evaluated tie molecule densities ( $f_{TS}$ ) decreased significantly with increasing composition of LMWPEs present in gel films of UL<sub>1</sub>, UL<sub>2</sub>, and UL<sub>3</sub> series. In addition,  $f_{TS}$  of the melt crystallized LMWPEs increase significantly with increasing lengths of short chain branches of LMWPEs. The achievable draw ratios of the gel films prepared from each weight ratio of LMWPE to UHMWPE approached a maximum value, when were prepared at concentrations close to their critical concentrations. These critical draw ratio ( $\lambda_c$ ) of gel films prepared near their critical concentrations were found to decrease significantly with increasing amounts of LMWPEs added in the gel films. However, addition of a small but optimum amount of LMWPE in gel films of UHMWPE/LMWPE blends can significantly improve their  $\lambda_c$  than that of gel film prepared from pure UHMWPE gel solution, and this improvement in  $\lambda_c$  is further enhanced with decreasing lengths of short chain branches of LMWPEs. This improvement in  $\lambda_c$  of these gel films is attributed to a suitable reduction of number of entanglements within gel films caused by addition an

optimum amount of a suitable branched lengths of LMWPE in UHMWPE/LMWPE blends. The tensile strengths, moduli and melting temperatures of these drawn gel films increase consistently with increasing draw ratio. The value of birefringence of these drawn films also increase consistently with the draw ratio, wherein the increasing rate of birefringence becomes slower as the draw ratio of the gel film is greater than about 40.

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