ELSEVIER

Polymer 40 (1999) 6859–6864

polymer

# Characterization of UHMWPE sol–gel transition by parallel plate rheometer and pulsed NMR

Hsien-Tang Chiu*, Jyh-Horng Wang

*Graduate School of Textile and Polymer Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10672, Taiwan*

Received 23 April 1998; received in revised form 30 September 1998; accepted 25 December 1998

## Abstract

The gel point and characterization of sol–gel transition of UHMWPE/decalin systems were investigated. In this study rheological method and DSC method were used to measure the gel point of UHMWPE gel at various concentrations. The result showed that the gel point increased with increasing gel concentration. Meanwhile pulsed NMR was also utilized to investigate 6 wt% UHMWPE gel. It was found that when sol–gel transition temperature was approximately 100°C, large amount of UHMWPE gel turned into solution state. Therefore, it produced re-entanglement and increased the random region within the UHMWPE molecular chain, which led to the decrease of interaction force among the polymer. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords*: Sol–gel transition; UHMWPE gel; Polymer

## 1. Introduction

UHMWPE fiber, is fabricated using gel spinning [1–3] to produce high strength fiber with extended chain structure. Therefore it is very important in the making of UHMWPE fiber to control preparation of optimum gel in gel-spinning process if one attempts to obtain an effective structure. However, the correlation between rheological behavior and formation of gel in sol–gel transition has not yet been investigated in detail. In previous studies, the UHMWPE gel was prepared by taking into consideration factors such as sufficiently high molecular weight, preparation of spinning dope, solvent, optimum concentration and, heating and stirring time. The solvents that have been used are decalin [4,5], paraffin oil [5,6], cycloakane [7] and xylene [8]. The type of solvent governs the result of UHMWPE gel formation and considerable differences have been observed. Matsuo et al. [9,10] formulated and proposed a relationship between molecular weight and gel concentration, and investigated correlation between draw ratio and fibers formed of various gel concentrations.

From the recent research by Zachariades [11,12], it is concluded that the UHMWPE gel cannot be considered as a true gel. In fact UHMWPE gel is a pseudo physical gel, which differs from a true gel, especially with respect to viscosity and temperature. The storage modulus of pseudo-gels decreases with increasing temperature. Ferry et al. [13] attributed the viscoelastic behavior of gel to the temporary entanglement of the molecular chains. Such a behavior is caused by the homogeneous network structure formed among the molecular chains [14]. Therefore, the entanglement density of the polymer will affect the flow behavior of the gel, which can be assessed by the flow curves. Such a gel does not flow without external force applied on it, hence the strain given to determine its viscoelastic characteristics should be small and within the linear viscoelastic strain range. The breaking of molecular chains of the gel can thus be avoided, and the characteristics and behavior of the gel may then be observed. The UHMWPE gel is a thermoreversible gel, belonging to the physical aggregation network under Flory's classification, [15], in which the crosslinks are formed by physical interactions. The networks formed through physical aggregation, are predominantly disordered, but with regions of local order. Viscoelastic properties change dramatically during the gelation process of a polymer solution: the system is liquid-like before crosslinking starts and remains a liquid till the viscosity becomes infinite at the gel point. The gel point of the UHMWPE gel is defined as transition from a solution to the gel state. According to the literature, the gel point can be determined using solubility [15], ball drop method [16], thermomechanical analysis [17], and differential scanning calorimetry (DSC) [17,18]. In this study the rheological method was employed to determine the gel point.

---

* Corresponding author. Tel.: +886-2-27376520; fax: +886-2-27376544.

PII: S0032-3861(99)00012-9

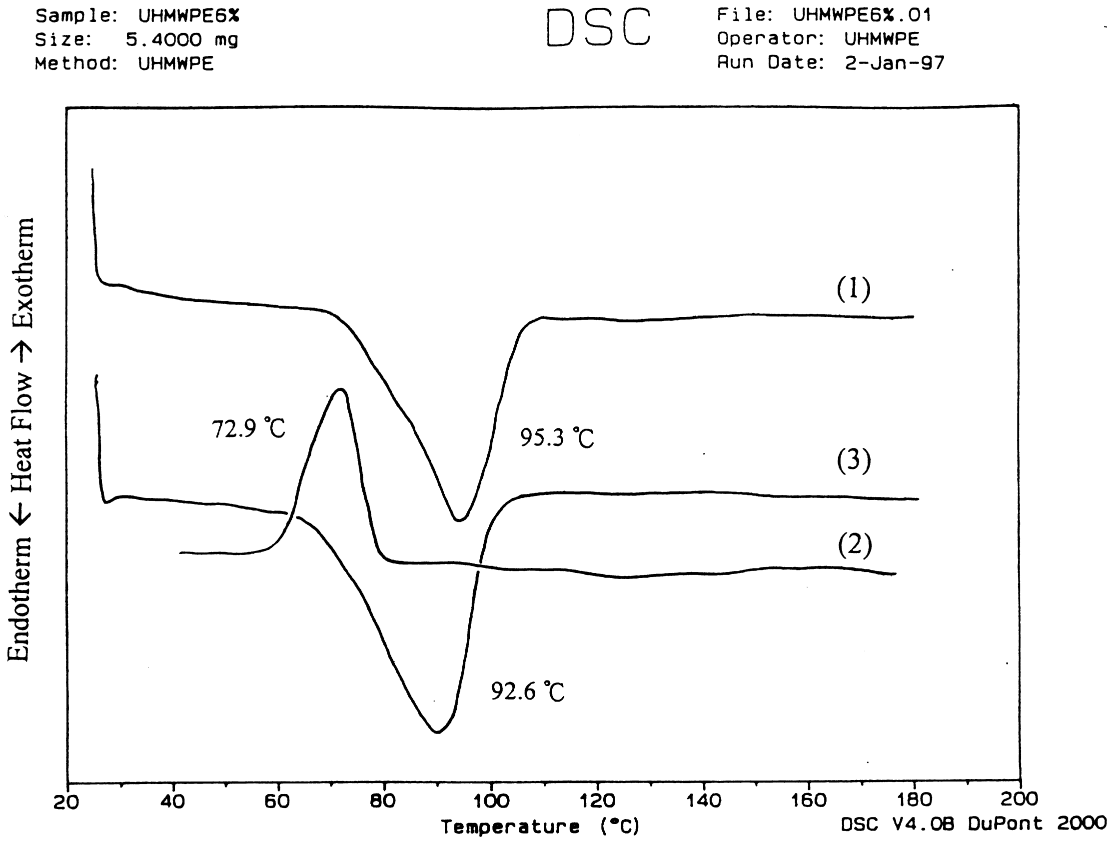

Fig. 1. DSC thermographs of UHMWPE gel at various concentrations.

Pulsed NMR is a powerful method to obtain the molecular mobility and the fractional amounts of heterogeneous phases in a sample. In previous research, pulsed NMR was applied to follow the gelation process in thermally different reversible gelling maltodextrin–water systems by Schierbaum et al. [19]. A marked change occurs in the signal with the formation of reversible gels, which depends on the temperature, concentration, time and structural peculiarities.

The structural morphology of the crystals of the UHMWPE gel under various concentrations in sol–gel transitions were investigated in an attempt to understand the interaction between the polymer and solvent, and also the formation mechanism of high strength fibers. DSC method was used to determine its gel melting point, which signifies crystallization effect. In addition parallel plate rheometer was used in rotation mode to measure its gel point and also to investigate its viscosity variation. Low resolution pulsed NMR was employed to determine transverse (spin–spin) relaxation times and decay curves using Carr–Purcell–Meiboom–Gill (CPMG) [20] method. The signal of pulsed NMR for a heterogeneous system is the super-position of different decay curves. One can obtain the mobility and the fractional amount of each phase by decomposing the signal. Moreover, the mobility of molecules at various temperatures (30°C–140°C), interaction between polymer and solvent, and the mobility near the sol–gel transition temperature were also investigated.

## 2. Experimental

The UHMWPE powder (USI Far Eastern Co., LTD; MW: $1.4 \times 10^6$ g/mol) was used in this experiment and the gel with concentrations of 2%, 4%, 6% and 7% was prepared using decalin as the solvent. In addition, di-*t*-butyl-*p*-cresol of 0.5 wt% (base to the polymer) was added as an anti-oxidant. The solutions were stirred at 150°C for 3 h under nitrogen atmosphere until the powder *dissolved completely* and the solutions were clear.

The crystallization, melting, and re-crystallization of UHMWPE gel could be investigated using differential scanning calorimeter model Dupont 2000. In this research UHMWPE gel with various concentrations (2%–7%) was scanned in a temperature range from 30°C to 200°C at a heating rate of 10°C/min. The 6 wt% UHMWPE gel underwent re-crystallization and second melting test at heating and cooling rate of 10°C/min and −10°C/min, respectively.

The rheological behavior was determined using parallel plate rheometer model Paar Physica US200. The measuring plate used was of the model MP30 ($r = 25$ mm, gap $= 1$ mm) and a solvent trap system was

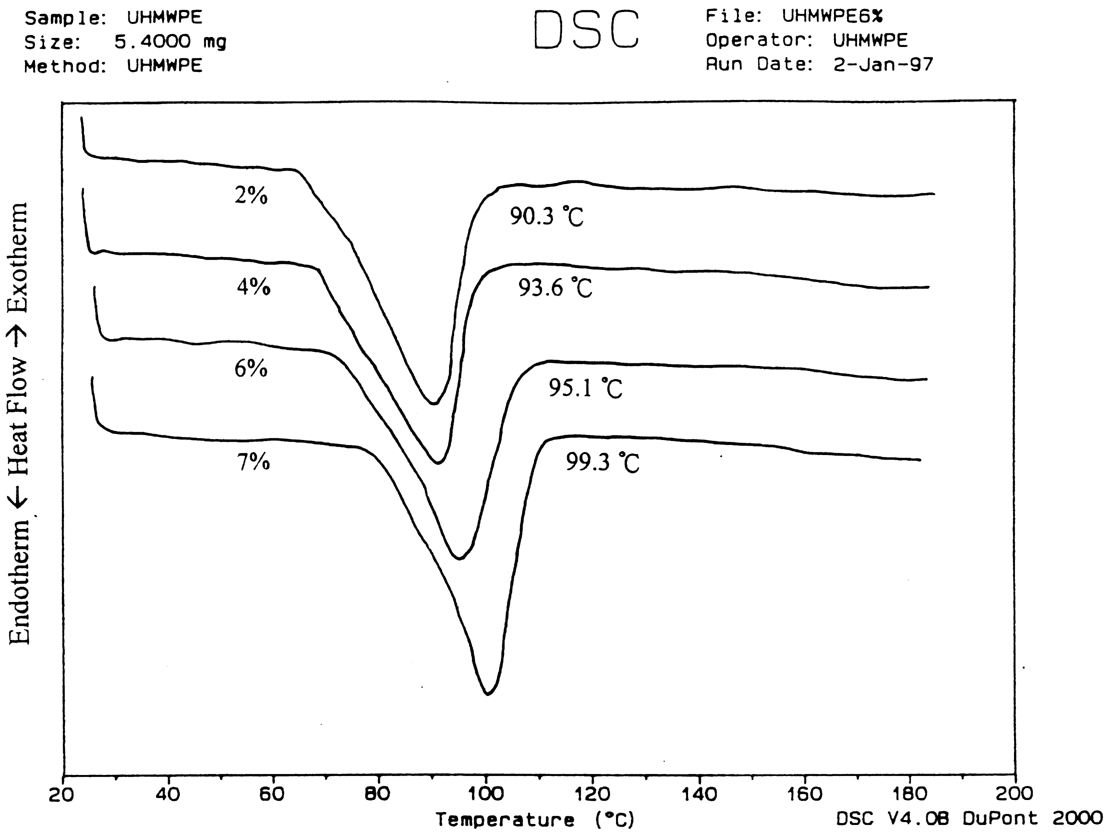

Fig. 2. DSC thermographs of 6 wt% UHMWPE gel.

utilized to avoid error from solvent evaporation. The gel point was determined in rotation mode with shear stress controlled at 100 Pa and in the temperature range 140°C–60°C. The relationship between the viscosity of the gel and the temperature was determined using a cooling process.

In low resolution 20 MHz NMR spectrometry, the quantity of hydrogen atoms in the sample, to be measured, is essentially constant. If a radio frequency pulse is applied for a few microseconds all the hydrogen nuclei are excited to rotate by 90° with respect to the static magnetic field. When the pulse is switched off they return to their original state, emitting an NMR signal. Hydrogen nuclei in the solid phase decayed more quickly than in the liquid phase. Meanwhile pulsed NMR was also used to investigate the characteristics of molecular mobility of UHMWPE gel under various temperatures in an attempt to understand the sol–gel transition.

$^1$H pulsed NMR measurements were performed with an MARAN-20 pulsed NMR spectrometer operating at a fixed frequency of 20 MHz at various temperatures (30°C–140°C). The 6% UHMWPE gel was placed in sealed glass tubes having an inner diameter of 12 mm, and then heated at various temperatures for 10 min. The recovery time of the spectrometer following a sequence of pulses was 13 μs. The measurement of spin–spin relaxation times, $T_2$ was carried out using CPMG pulsed sequence $[90°x\tau(180°y2\tau)n]$ ($p90° = 2.9$ μs, $p180° = 5.8$ μs and $n = 2000$) available for long $T_2$ sample.

## 3. Results and discussion

The melting and the crystallization behavior of UHMWPE gel could be understood from Figs. 1 and 2. Fig. 1 shows DSC curves of UHMWPE gel with various gel concentrations. Each curve shows a distinct endothermic peak which corresponds to the gel melting point of UHMWPE gel. In addition, the gel melting point increases from 90.3°C to 99.3°C as gel concentration increases from 2% to 7%. Such an increase is the result of a large domain resulting from more molecular entanglement density, which is the result of more chain aggregation with gel of higher concentration. This phenomenon suggests an increase in molecular interaction force with increasing number of molecular chains from an increase in solute concentration. Fig. 2 depicts the re-crystallization and re-melting curve of 6 wt% UHMWPE gel. The first melting curve shows an endothermic peak at 95.1°C. The re-crystallization temperature test was then performed on the same sample at a cooling rate of −10°C/min. The result shows that there is an exothermic peak at 72.9°C, which is then known to be its re-crystallization temperature. The second melting test was performed later at a heating rate of 10°C/min and the

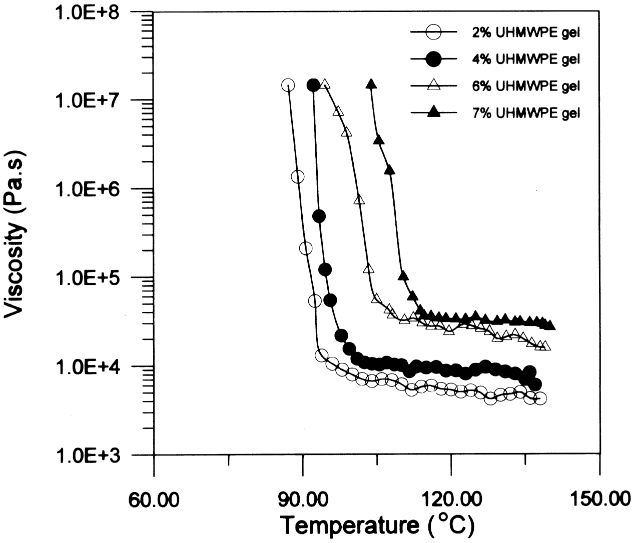

Fig. 3. The relationship between the viscosity and the temperature for UHMWPE gel at various concentrations.

outcome of the test shows a gel melting point of 92.6°C. From this experiment it is concluded that the reason for obtaining a higher first melting point is because of the stirring in the dissolving process of the gel, which leads to a change in the crystal morphology. In contrast, as this sample was molten in its re-crystallization process in which it was not subjected to any shear force, the crystals were therefore formed in a static condition. The crystals formed in this process are thus known as single crystals whose melting point goes down slightly. Fig. 3 shows the viscosity of UHMWPE gel with various concentrations against temperature. It is observed that the viscosity increases with decreasing temperature for every curve. It is also found in solution state (at plateau region) of UHMWPE gel that the viscosity increases with increasing gel concentration. As the test was performed when the temperature decreased, the temperature at gel point is also the point of inverse of sol–gel transition caused by gelation. From the appearance of the gel it was found that the gel was changed from a transparent state to a turbid state, in this transition, accompanied by a phase separation. When it became opaque and was of a turbid texture, and consisted of stacks of single crystals and large spherulitic crystals, the viscosity of the gel increased abruptly. In addition, it is also found that the gel point increases with increasing gel concentration. Such a phenomenon can be further explained using Fig. 4 which depicts the relationship between the concentration and the gel point by the rheological and the DSC methods. It is shown in this figure that both the gel point and gel melting point increase

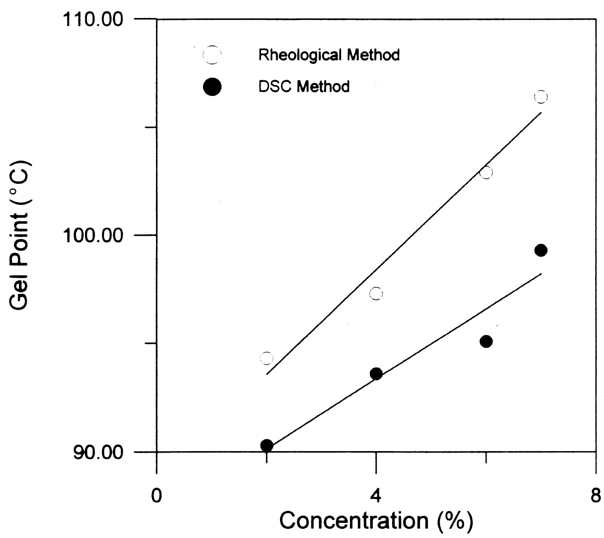

Fig. 4. The relationship between the gel points and various UHMWPE gel concentrations.

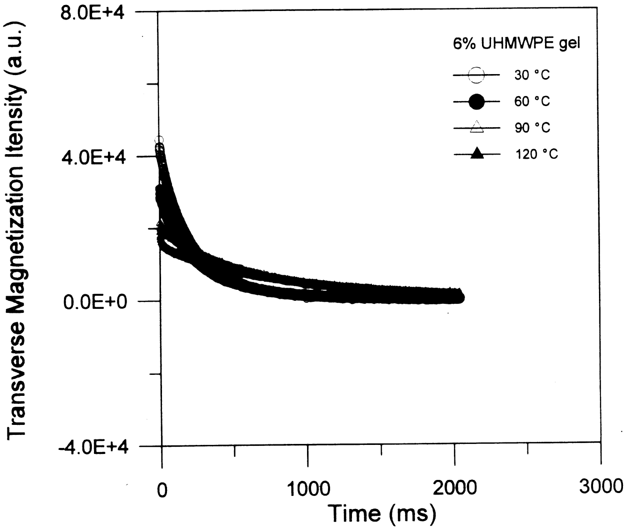

Fig. 5. The decay curves of 6% UHMWPE gel at various temperatures.

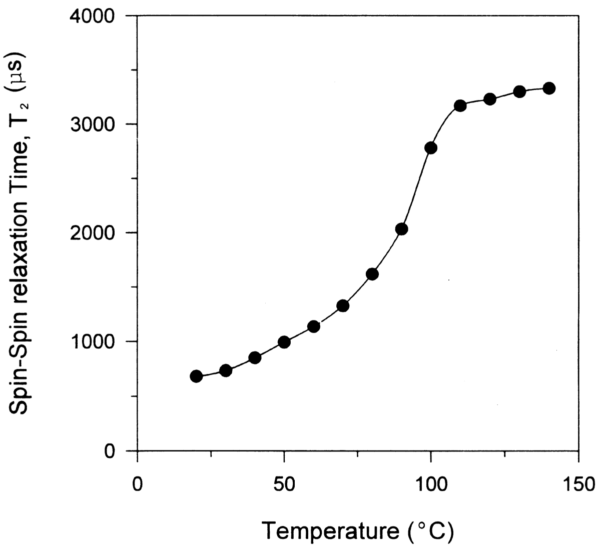

Fig. 6. The relationship between the spin–spin relation time and temperature for 6% UHMWPE gel.

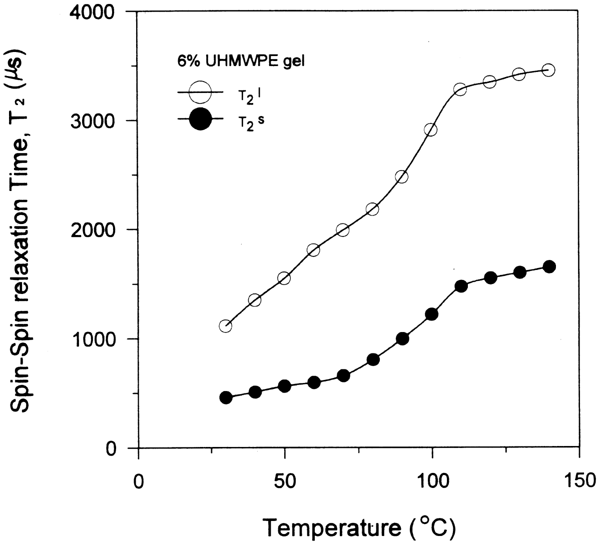

Fig. 7. The relationship between the spin–spin relation time of each component and temperature for 6% UHMWPE gel.

with increasing gel concentration. The reason why the gel point increases with increasing gel concentration is that a gel of a higher concentration produces higher molecular entanglement density. This phenomenon suggests the increase in molecular interaction force with increasing number of molecular chains from an increase of solute concentration.

Fig. 5 shows the CPMG decaying signal of 6% UHMWPE gel at various temperatures. From this figure it is seen that as temperature increases, decaying signal curves tend to become flat. Such behavior indicates that transverse magnetization intensity changes gradually from the solid phase to the liquid phase. Therefore, the solid signal decays gradually in contrast to the liquid signal intensity in this process. Using the results of Fig. 5, we obtain Fig. 6 which shows the curve of spin–spin relaxation, $T_2$, at various temperatures. From Fig. 6 it is observed that the liquid signal strengthens as the temperature increases. In the NMR spectrum it is seen that the hydrogen nuclei in the solid phases decay more quickly than those from liquids. Therefore, as $T_2$ increases, liquid phases are seen to increase. In addition, a point of inversion occurs at approximately 100°C, which is known as the gel point, i.e., sol–gel transition temperature. In this figure it is found that a large amount of gel turns to solution state as temperature increases up to this point of inversion. It is also seen that the gel point obtained using this method is nearly identical to that obtained in the rheological method, but higher than that in the DSC method. Further, the CRMG decaying signal of all the samples are decomposed into two components for calculating $T_2$ and the fractional amount, $f$, of each component [21]. Fig. 7 shows the $T_2$ of each component for 6% UHMWPE gel at various temperatures. In this figure a long $T_2^{\mathrm{l}}$ represents the relaxation time of polymer poor phases while a short $T_2^{\mathrm{s}}$, the relaxation time of polymer rich phases. It is seen from the figure that as the temperature increases, $T_2^{\mathrm{l}}$ also increases. When the temperature reaches the sol–gel transition temperature, its increasing rate reaches the maximum. At a higher temperature this transition temperature, $T_2^{\mathrm{l}}$ reaches an equilibrium state, which indicates that the gel has turned itself completely to the solution state. Therefore, the $T_2^{\mathrm{s}}$ curve displays the same characteristics. The reason why $T_2^{\mathrm{s}}$ increases with increasing temperature before coinciding with the sol–gel transition temperature is that the larger disorder and free volume of molecular chains lead to less chain aggregation. As the temperature reaches the sol–gel transition point, the $T_2^{\mathrm{s}}$ increasing rate reaches the maximum value, and then $T_2^{\mathrm{s}}$ reaches an equilibrium state gradually. This is because all polymer rich phases become polymer poor phases; such a result is symmetrical to that of $T_2^{\mathrm{l}}$. Fig. 8 shows $f$ values of each component of 6% UHMWPE gel at various temperatures. From this figure it is seen that the fraction amount ($f^{\mathrm{l}}$) of polymer poor phases increases with increasing temperature, and later reaches equilibrium. In contrast the fraction amount ($f^{\mathrm{s}}$) of polymer rich phases decreases with increasing temperature and reaches an equilibrium at the sol–gel transition point. This makes the transition of polymer rich phases to polymer poor phases possible and hence an increase of $T_2$ occurs.

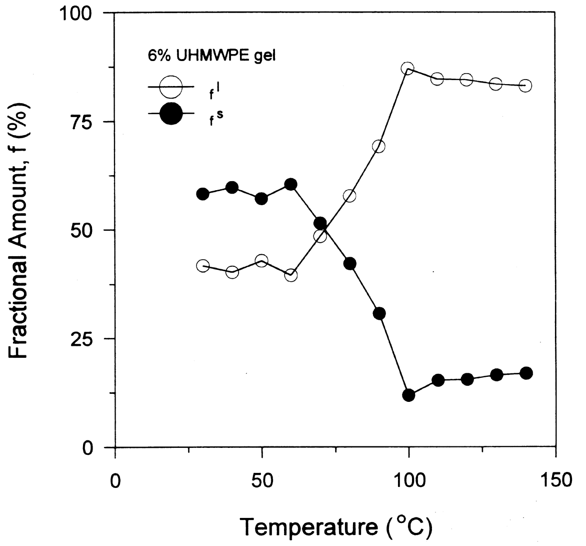

Fig. 8. The relationship between the fraction amount of each component and temperature for 6% UHMWPE gel.

## 4. Conclusion

The formation of the UHMWPE fiber is closely linked to the preparation of its gel while the formation of gel is subject to factors such as gel concentration, molecular weight, type of solvent, heating and stirring time, and temperature. In this article the phase transformation point of the sol–gel transition was studied with an attempt to find the relationship between the gel point and the gel concentration at this transformation point. The result shows that the gel point increases with increasing gel concentration. Also the trend of the increase observed from the rheological method is the same as that in the DSC method. Further, pulsed NMR was utilized to investigate the effect of temperature on $T_2$ in an attempt to comprehend the characteristics of the sol–gel transition. It is found that the solid signal decreases dramatically and the liquid signal increases at around 100°C. In contrast, $T_2^{\mathrm{l}}$ increases with increasing temperature and the increase in rate reaches a maximum when the temperature reaches the sol–gel transition temperature. At temperatures higher than the transition temperature, $T_2^{\mathrm{l}}$ reaches equilibrium gradually. For polymer rich phases, $T_2^{\mathrm{s}}$ increases with increasing temperature and then reaches equilibrium gradually. The reason why $T_2^{\mathrm{s}}$ increases with increasing temperature before the sol–gel transition point is that a larger disorder and free volume lead to less chain aggregation, and all polymer rich phases then turn into polymer poor phases. Also $T_2^{\mathrm{s}}$ reaches an equilibrium state gradually.

## Acknowledgements

We thank the National Science Council of Taiwan for support for this work under the project NSC-85-2216-E-011-010.

## References

[1] van Hutten PF, Koning CE, Smook J, Pennings AJ. Polym Commun 1983;24:237.
[2] Kalb B, Pennings AJ. Polymer 1980;21:3.
[3] Barbam PJ, Keller A. J Mater Sci 1985;20:2281.
[4] Smith P, Lemstra PJ. J Mater Sci 1980;15:505.
[5] Kalb B, Pennings AJ. Polymer 1980;21:3.
[6] Kavesh S, Prevorsak DC. US Patent, 4 413 110, 1983.
[7] Chen WL, Lee DM, Chen LT, Yeh MT. US Patent, 5 342 567, 1994.
[8] Wang XY, Salovey R. J Appl Polym Sci 1987;34:593.
[9] Sawatari C, Okumura T, Matsuo M. Polym J 1986;18(10):741.
[10] Ogita T, Yamamoto R, Suzuki N, Ozaki F, Matsuo M. Polymer 1991;32(5):822.
[11] Zachariades AE. J Appl Polym Sci 1986;32:4277.
[12] Chung B, Zachariades AE. ACS Polym Rep 1986;27(1):208.
[13] Nizomiya K, Ferry JD. J Polym Sci, Part A-2 1967;5:195.
[14] Ferry JD. Viscous properties of polymers, New York: Wiley, 1980.
[15] te Nijenhuis K. Adv Polym Sci 1997;130:1.
[16] Takahashi A, Sakai M, Kato T. Polym J 1980;12(5):335.
[17] Jo WH, Kwon IH, Seoul C. Polym Engng Sci 1989;29(22):1569.
[18] Chiu HT, Wang JH. Chine. J Mater Sci 1997;31:1.
[19] Schierbaum F, Radosta S, Vorwerg W, Yuriev VP, Braudo EE, German ML. Carbohydrate Polym 1992;18:155.
[20] Meiboom S, Gill D. Rev Sci Instrum 1958;29:688.
[21] Hong PD, Chen JH, Wu HL. J Appl Polym Sci 1999: in press.