Morphology and mechanical properties of ultrahigh-molecular-weight polyethylene prepared by gelation/crystallization at various temperatures

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Films of ultrahigh-molecular-weight (3×10^6) polyethylene were produced by gelation/crystallization at various temperatures from dilute decalin solutions according to the method of Smith and Lemstra. The temperatures chosen were 20, 30, 50 and 70°C. With increasing temperature, the long period and crystallinity of the resultant gel film increased. By contrast, when the films were stretched up to 300 times, the increases in Young's modulus, crystallinity and molecular orientation become more significant as the temperature of gelation/crystallization become lower. This interesting phenomenon is thought to be due to the dependence of the number of entanglement meshes on the temperatures of gelation/crystallization and evaporation of solvent from the gel to form a film.

(Keywords: polyethylene; gelation/crystallization; temperature effect; Young's modulus; molecular orientation; entanglement)

INTRODUCTION

Recently, Smith *et al.* have demonstrated that the effective drawability of high-molecular-weight polyethylene is dramatically enhanced by using specimens spun or cast from semidilute solutions to form macroscopic gels[1]. This method has been developed by Smith and Lemstra[2–4]. It was found that for a sufficiently high molecular weight the maximum achievable draw ratio depended principally on the concentration of the solution from which the gel was made[3]. This phenomenon was attributed to a reduced number of entanglement meshes per molecule in solution-cast/spun polymers in comparison with those obtained from the melts[3,5].

According to their report[2], the as-spun liquid filament was quenched in cold water to form a gel fibre or the extremely viscous concentrated solution containing 10% w/w of polyethylene was compression-moulded into a sheet and subsequently quenched to room temperature[4]. The quenching process has been thought to play an important role to assure high drawability to prepare high-modulus and high-strength fibres or films. This concept is based on the assumption that the reduced number of entanglements per molecule in solution remains within the resultant gel films through the quenching and drying processes. This assumption has been accepted but is not still demonstrated.

This paper focuses on whether or not quenching causes a significant effect on the preparation of high-modulus and high-strength polyethylene fibres and films. The samples were prepared by gelation/crystallization at various temperatures from solutions. The estimation is carried out in terms of morphological and mechanical aspects.

EXPERIMENTAL

The sample used in this experiment was linear polyethylene, Hizex Million 240M, with viscosity-average molecular weight of 3×10^6 and negligible degree of branching. This linear polyethylene was furnished as a powder by Mitsui Petrochemicals Co. Ltd. The solvent was decalin. A decalin solution containing 0.65 g/100 ml of polyethylene and 0.1% w/w of the antioxidant di-t-butyl-*p*-cresol was prepared by heating the well blended polymer–solvent mixture at 135°C for 40 min under nitrogen. Through previous experiments[5], it has been found that a concentration of 0.65 g/100 ml assures the greatest significant drawability of the resultant dry gel film prepared by gelation/crystallization at 0°C and evaporating solvent at 20°C. The possibility of successfully drawing up to draw ratio $\lambda = 300$ becomes lower as the concentration is away from 0.65 g/100 ml. The hot homogenized solution was quenched by pouring into an aluminium tray that was surrounded by a poly(ethylene glycol) (PEG) bath at the desired temperature. The decalin was allowed to evaporate from the gel in the aluminium tray after crystallization. The resulting 300 μm dry gel film was immersed in ethanol and subsequently

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air dried to remove residual traces of the decalin–ethanol mixture.

The specimens were characterized by density, X-ray and load–elongation. These methods have already been described elsewhere[6–9].

RESULTS AND DISCUSSION

Figure 1 shows the macroscopic structure of a gel prepared by crystallization in a beaker surrounded by PEG at 80°C. It is seen that the gel is not uniform and shows phase separation. When the solvent was evaporated at 80°C, the resultant dry gel could not form a uniform film.

Figure 2 shows the WAXD and SAXS patterns of the gel film prepared by quenching at 70°C, when the incident beam was directed parallel to the film surface (end view). Similar profiles of the two patterns were observed for the gel film prepared by quenching at 0°C[5]. Accordingly, it is evident that, even on quenching at 70°C, the resultant gel film is composed of crystal lamellae that are highly oriented with their large flat faces parallel to the film surface and within the lamellae the *c* axes are oriented perpendicular to the large flat faces[9–12].

Table 1 lists the crystallinity, long period and lamellar thickness calculated from the crystallinity of the films prepared by gelation/crystallization and evaporation of decalin at the indicated temperatures. The crystallinity was calculated from the density, by assuming densities of the crystal and amorphous phases to be 1.000 and 0.852 g cm^{-3}, respectively[13]. Interestingly, the crystallinity and long period increase with increasing temperature. This is in good agreement with the conventional concept that the mobility of molecular chains becomes more pronounced as the temperature of gelation/crystallization becomes higher, and then this effect causes further decrease in few coupling entanglements associated with predominantly intermolecular in solution by wigging out of chains during the crystallization process. Furthermore, the increase in the resultant lamellar thickness becomes slightly pronounced through evaporation of decalin at 70°C because of isothermal crystallization. Therefore the increases in lamellar thickness and crystallinity are more pronounced as the temperature increases up to 70°C. Beyond 80°C, the number of coupling entanglement meshes is thought to be extremely small and the crystal lamellae formed by such random coils are similar to single-crystal mats.

Figure 3 shows the change in the appearance of undrawn gel films under scanning electron microscopy. The specimens were prepared by gelation/crystallization from solutions and by evaporating solvent at the indicated temperatures. Close observation reveals that the morphology of fibrillar textures is almost independent of the temperature of gelation/crystallization. Namely, in all the undrawn films, the fibrillar texture appears to be

Table 1 Crystallinity, long period and thickness of crystal lamellae for the dried gel films prepared at the indicated gelation/crystallization temperatures in an undeformed state

Gel./cryst. temp. (°C)	Crystallinity (%)	Long period (Å)	Thickness of crystal lamellae (Å)
quench/20	83.0	114	95
30	83.0	114	95
50	86.5	120	104
70	87.1	124	108
80	87.7	135	118

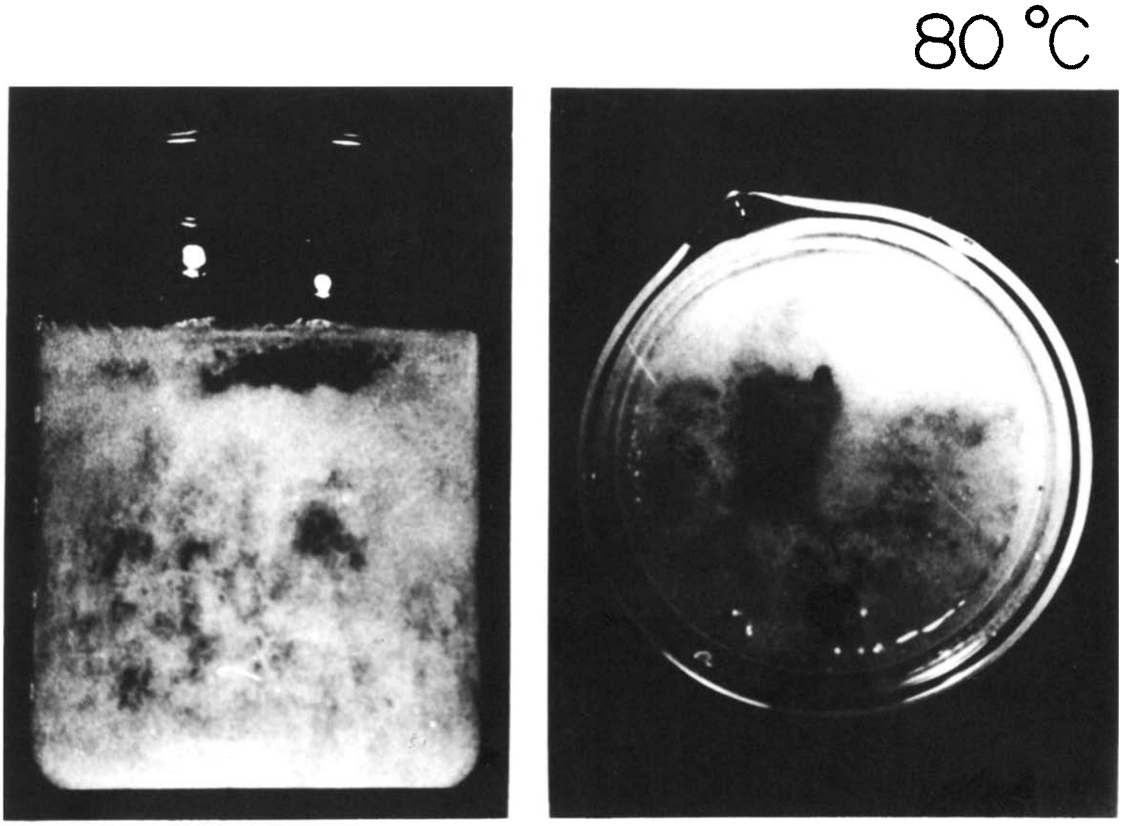

Figure 1 Macroscopic structure of gel prepared by crystallization at 80°C

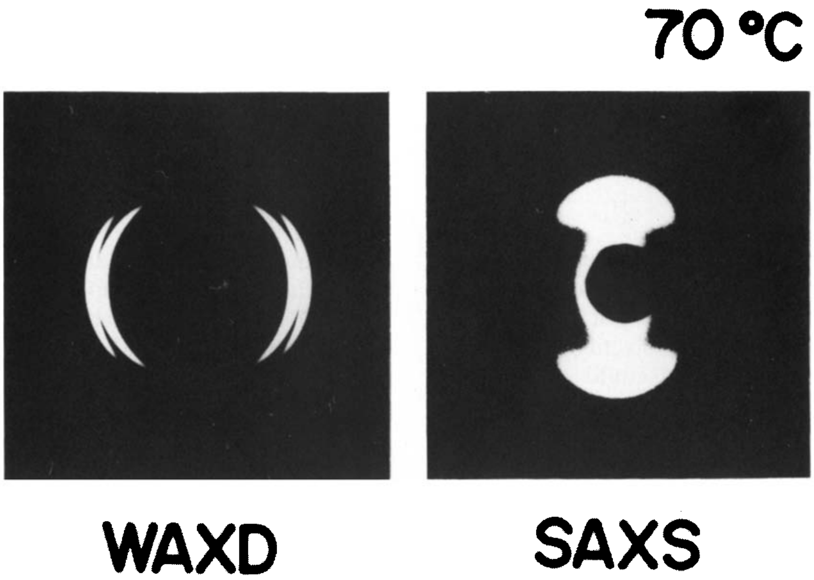

Figure 2 WAXD and SAXS patterns (end view) from a gel film prepared by evaporating decalin at 70°C

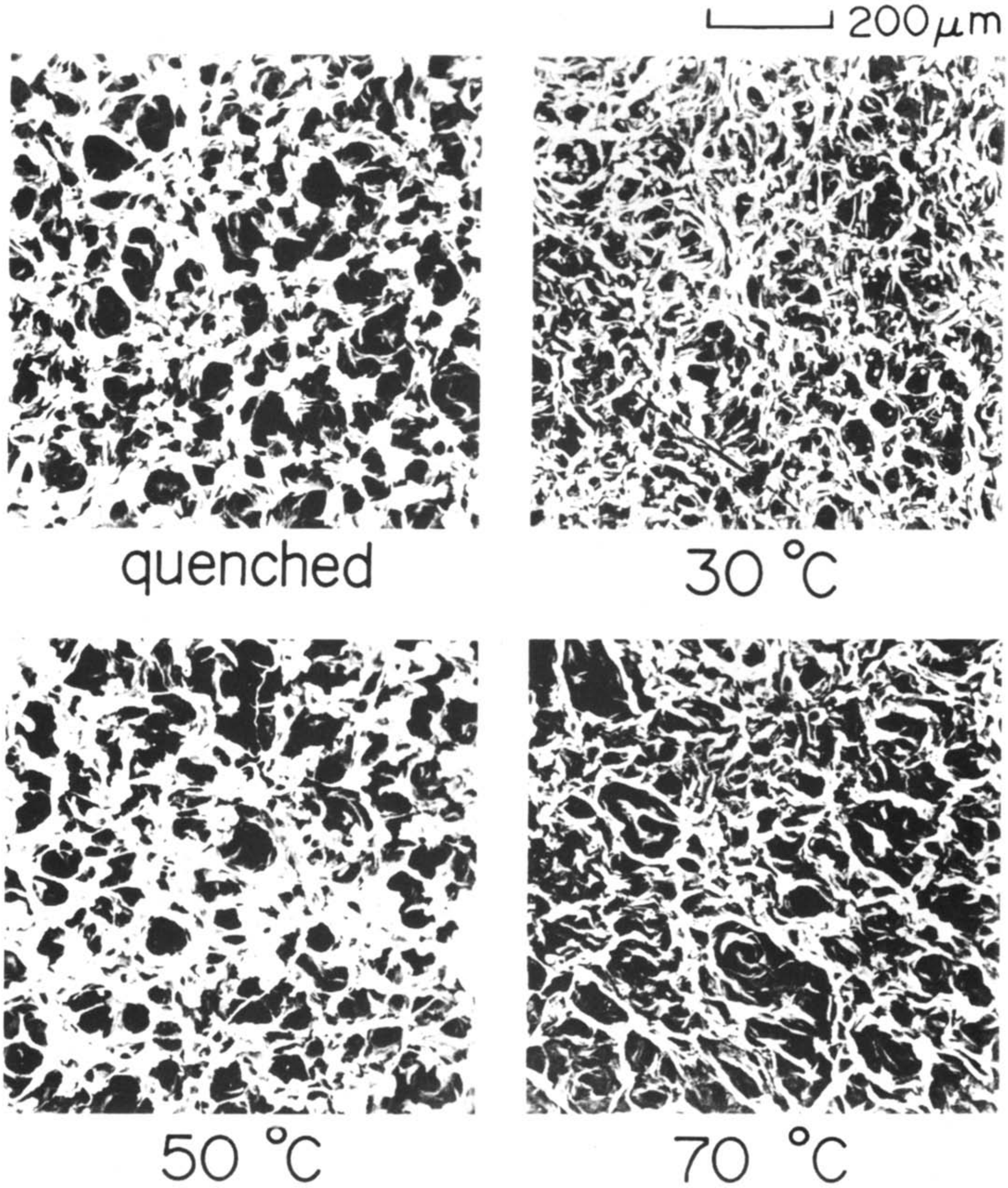

Figure 3 Scanning electron micrographs of the undrawn films prepared by gelation/crystallization at the indicated temperatures

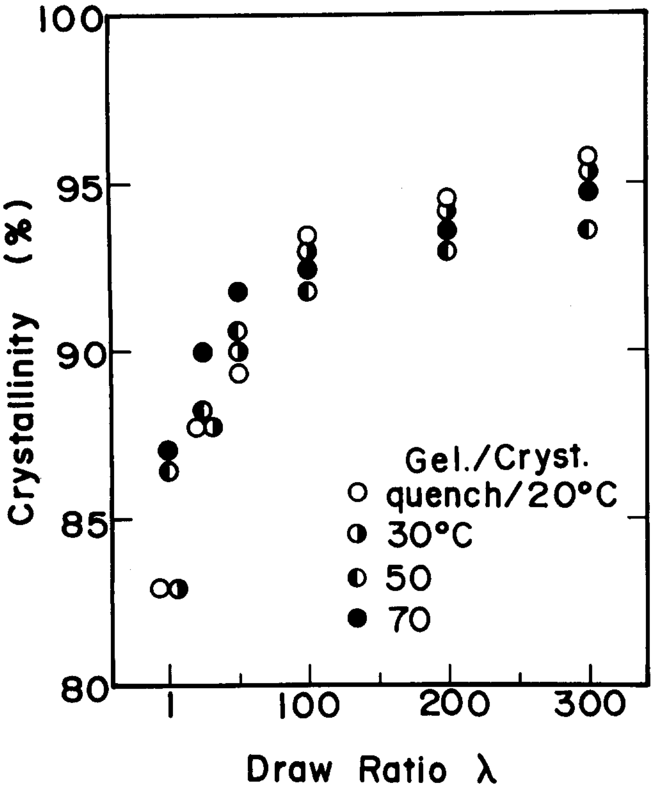

Figure 4 Crystallinity as a function of the draw ratio λ for the gel films prepared by gelation/crystallization at the indicated temperatures

a spongy tissue comprised of interconnected lamellar crystals. When the samples are stretched, observation reveals that the crosslinking loci consist of fibrillar shish-kebab-like crystals arranged in the draw direction, as has been reported elsewhere[14–16].

Figure 4 shows the change in crystallinity with increasing draw ratio λ. The crystallinity was calculated by assuming that the intrinsic densities of crystal and amorphous phases are constant in spite of molecular orientation and crystal transformation from a folded to a fibrous type, and then the change in density of film is attributed to an increase in crystallinity. It may be noted that up to $\lambda = 50$, the crystallinity of the specimen prepared by evaporating decalin at 70°C takes the highest value and the crystallinity decreases on decreasing the temperature of gelation. Beyond $\lambda = 100$, however, the increase in crystallinity of the specimen prepared by evaporating decalin at 20°C becomes considerable with draw ratio and the value reached 96% at $\lambda = 300$. This is probably due to the fact that the specimen prepared by quenching in an ice-water bath and evaporating decalin at 20°C has the most suitable number of entanglement meshes. Namely the concentration, 0.65 g/100 ml, corresponds to the critical one to prepare the gel by crystallization in ice-water in order to assure the most favourable possibility of successfully drawing up to $\lambda = 300$[5]. But, as discussed before, the gelation/crystallization from decalin solution at elevated temperature causes a decrease in the most suitable number of entanglement meshes. Thus it may be expected that slippage of molecular chains occurs for the specimen prepared by gelation/crystallization beyond 50°C as draw ratio increases beyond $\lambda = 100$.

To support the above concept, the second-order orientation factor, F_c, of the c axis with draw ratio was obtained for the specimens prepared by quenching and subsequently evaporating decalin at the indicated temperatures. This result is shown in *Figure 5*. F_c characterizes the orientation distribution of the c axes, with variation between $-1/2$ and 1. For random orientation, F_c is 0, while for complete orientation parallel and perpendicular to the stretching direction, F_c is unity and $-1/2$, respectively. The orientation factor was estimated directly from the orientation distribution function of the (0 0 2) plane. An increase in the orientation factor of the specimen prepared by quenching at 0°C and evaporating decalin at 20°C is the most significant and the orientation factor at $\lambda = 300$ decreases with increasing temperature of gelation/crystallization. This indicates that a decrease in the number of entanglement meshes when evaporating decalin at elevated temperature hampers the perfect orientation of the c axes, because of slippage of molecular chains. This result supports the birefringence data in *Figure 6*. A considerable increase in birefringence with increasing λ can be observed for the specimens prepared by quenching in an ice-water bath and evaporating decalin at 20°C.

Figure 7 shows the change in the Young's modulus as a function of draw ratio λ for the gel films prepared by evaporating decalin at the indicated temperatures. The increase in the Young's modulus with increasing λ beyond 100 times is the most significant for the film quenched at 0°C and solvent evaporated at 20°C. This is a reasonable result, since the crystallinity, the second-order orientation factor and birefringence of this specimen take the highest values among the given specimens at $\lambda \geq 100$. This implies that the change in initial entanglement density due to an increase in temperature of gelation/crystallization causes a significant effect on the Young's modulus of drawn films. This supports the concept of Smith and Lemstra that the number of entanglements per molecule remains within the resultant gel films

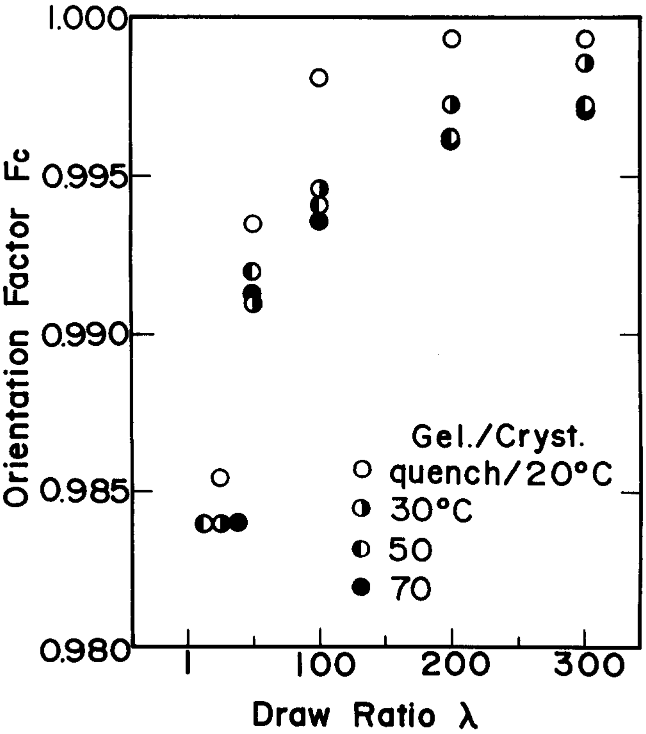

Figure 5 The second-order orientation factor of the c axis as a function of the draw ratio λ for the gel films prepared by evaporating solvent at the indicated temperatures

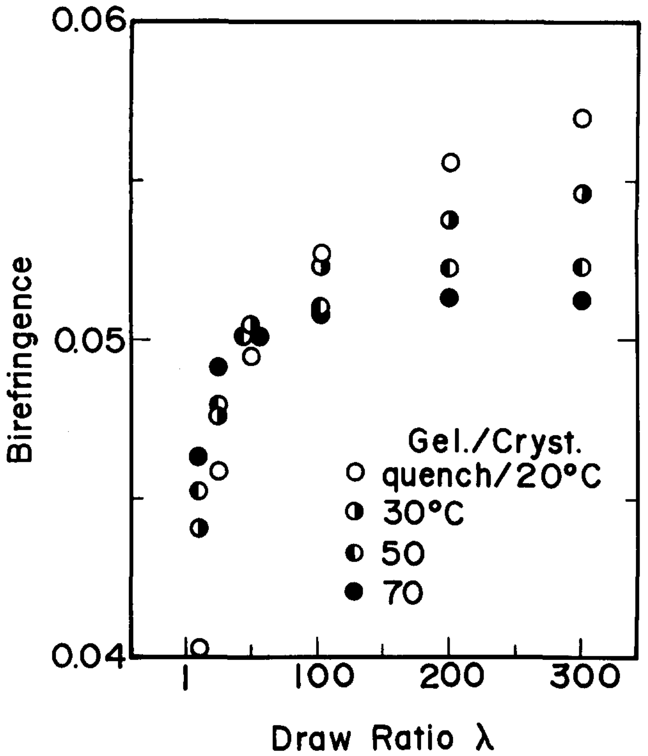

Figure 6 Birefringence as a function of the draw ratio λ for the gel films prepared by evaporating solvent at the indicated temperatures

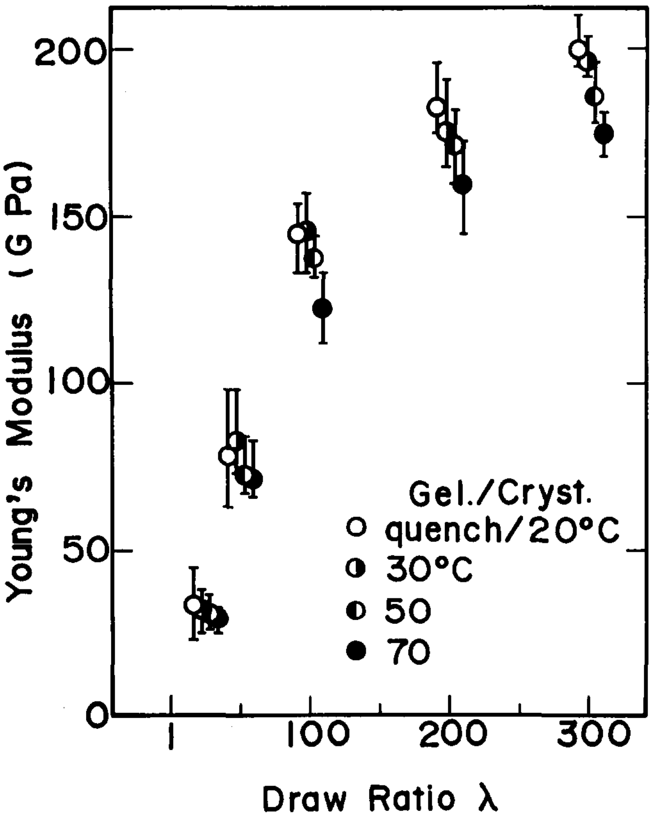

Figure 7 Young's modulus as a function of the draw ratio λ for the gel films prepared by evaporating solvent at the indicated temperatures

through quenching in an ice-water bath and drying at room temperature[3].

CONCLUSIONS

Hot homogenized polyethylene solution was quenched by pouring it into an aluminium tray that was surrounded by an ice-water or a PEG bath with various temperatures and subsequently the solvent was evaporated from the gel at desired temperatures beyond 20°C. The concentration was set to be 0.65 g/100 ml, corresponding to the critical one to assure the most favourable successful drawing up to $\lambda = 300$ in the case when the gel was crystallized at 0°C and the solvent was evaporated at 20°C. Flat gel films could not be formed at temperatures beyond 80°C. The crystallinity and long period for original films prepared at 70°C are the highest due to the effect of isothermal crystallization, but the increases in both values with increasing draw ratio were the most significant for the films prepared by evaporating decalin at 20°C after gelation/crystallization in an ice-water bath. That is, this specimen provides the highest values of the Young's modulus, crystallinity and second-order orientation factor of the *c* axes at $\lambda = 300$. In contrast, these corresponding values were less pronounced as the temperature of crystallization to form gels increases. This is probably due to a decrease in the number of suitable entanglement meshes within the resultant dried film. Such a decrease causes slippage of molecular chains under elongation beyond $\lambda = 100$. This behaviour hampers the improvements of the Young's modulus and molecular orientation.

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