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Gelation behaviour of UHMWPE/camphene

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The sol–gel transition behaviour of ultra-high molecular weight polyethylene (UHMWPE) in decalin, paraffin oil and camphene has been investigated. UHMWPE solutions exhibit a thermo-reversible gelation, recognized in gels, which is due to crystallization. Viscosity results indicated that polymer molecules disentangled more easily when camphene was used as a solvent. This characteristic implies that camphene is a more desirable solvent for solution processing of UHMWPE. A higher recrystallization temperature, T_c, also occurred at a higher gelation temperature, T_{gel}. The gel melting temperature, $T_{m,gel}$, was also measured and its dependency on polymer concentration was investigated using the Eldridge–Ferry equation. The reciprocal of the absolute gel melting temperature was found to have a linear relationship with the logarithm of polymer concentration

1. Introduction

The gel-spinning process of ultra-high molecular weight polyethylene (UHMWPE) has been the subject of recent interest for producing high-strength and high-modulus fibres from a semi-diluted solution of flexible-chain polymers [1–3]. Among these, UHMWPE fibre has found successful commercial application by DSM [4–6], Allied-Signal [7, 8], as well as several fibre producers in Japan [9, 10]. Most current studies now, therefore, focus on the relationship between structure and properties of UHMWPE gel [11, 12]. Conventional melt-processing methods are unsuitable for these materials, because of the very high melt viscosity associated with an extremely high molecular weight. Consequently, solution processing becomes a desirable step. A gel provides a means of decreasing the density of chain entanglement by dissolution, which is essential to maximize the draw ratio in the hot-drawing of a fibre. Properties of the polymer solution and, subsequently, the gel after cooling, depend upon factors such as the kind of solvent, the operating temperature and polymer concentration. The sol–gel transition of crystalline polymers is thermally reversible, and the structure of a crystalline gel is essentially different from a gel whose network is formed by a covalently crosslinked amorphous chain [13, 14]. UHMWPE has recently become a popular topic because its gel exhibits excellent spinnability; in addition, fibres obtained by drawing of the gel generally have a high strength and modulus [15]. Conversion of a polymer solution to a gel should cause the formation of cross-linking junction point in the gel. According to the viscoelastic behaviour of the solution, the structural features of the gel and the gelation mechanism on cooling, have increasingly become the emphasis of research in recent years, e.g. thermal history, crystallization gel morphology and rheological properties of PE solutions and gels [6–25]. Nevertheless, the mechanism of sol–gel transition and the morphological structure of the PE gel remain not fully understood.

In this study, the rheological and thermoreversible gel behaviour of UHMWPE were investigated in three solvents, i.e. decalin, paraffin oil and camphene [22]. In particular, the relation between crystallization and gelation, along with the mechanism of gelation, were studied.

2. Experimental procedure

The polymer material used in this study was the Hostalen GUR linear UHMWPE powder with $\bar{M}_w = 1.5 \times 10^6$. The solvents employed were decalin, paraffin oil and camphene. Decalin and paraffin oil are currently used in commercial processes by DSM and Allied Signal, respectively. Camphene is a novel solvent discovered at the Union Chemical Laboratories. These solvents were used as-received without further purification. The concentration of the polymer solution varied from 10–100 $\mathrm{g\,l^{-1}}$. Preparation of these solutions was carried out by mechanical stirring at 150 °C for at least 5 h to obtain a macroscopically homogeneous solution. Additionally, 2 wt % 2,6-Di-*t*-butyl-*p*-cresol was added to the solution as an antioxidant.

2.1. Viscosity

A rotating viscometer (Brookfield RV-DV III) was used to establish the relationship between the apparent viscosity and the shear rate of the PE solution. The solutions were allowed to reach thermal equilibrium at a fixed temperature before measurements were taken. The gelation temperature was obtained by measuring the sharp increase of viscosity

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during cooling of the solution at a cooling rate of 1 °C min^{-1} and at a shear rate of 1 s^{-1}.

2.2. Differential scanning calorimetry

The thermograms were obtained by a Shimadzu DSC-50. Samples were flushed with a nitrogen stream during each scan. In each run, 15–20 mg gel samples were placed in a liquid pan and sealed tightly before scanning. The heating rate and cooling rate were both set at 5 °C min^{-1}.

2.3. X-ray diffraction

Wide-angle X-ray patterns were obtained using a Laue camera (MAC Sciences, Japan) with nickel-filtered CuK_α radiation at 30 mA and 35 kV.

2.4. Morphological observation

The morphology of each gel was observed using a Zeiss Universal polarized microscope equipped with crossnicols and a Leitz model 350 hot stage. In the operation, the gel sample was carefully placed in a glass desk during the hot stage, and then redissolved by heating. The solution was maintained at 180 °C for 30 min, then cooled slowly to 80 °C and held for 20 min. A scanning electron microscope was used to visualize the microstructure of UHMWPE fibre.

3. Results and discussion

The properties of a polymer solution are very important for gel spinning of UHMWPE. Three solvents were investigated in this study, i.e. decalin, paraffin oil and camphene. Fig. 1 shows the relation between solution viscosity and shear rate in these solvents for UHMWPE. This figure indicates that the viscosity of UHMWPE/camphene solution is the lowest. When polymeric molecules are entangled in the fluid, a high entanglement density can increase the interaction between the molecular segments. This interaction occurs in an undesirable flow behaviour [17, 19]. A lower viscosity would allow the polymer to be processed and disentangled more easily in camphene.

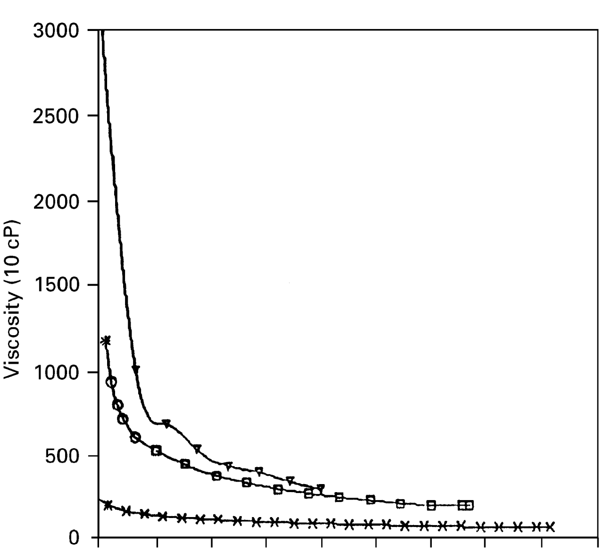

Figure 1 Relation between solution viscosity and shear rate of 2 wt % UHMWPE in various solvents at 135 °C; (▽) decalin, (□) paraffin oil, (×) camphene.

The solutions of UHMWPE in decalin, paraffin oil and camphene transform to a gel on cooling. These gels also redissolve into solution form upon heating. These observations confirm the theory that the sol–gel transition is thermoreversible in nature. Conversion of a polymer solution to a gel should cause the formation of a three-dimensional network or cross-linking junction points in the gel. Takahashi *et al.* [27] proposed that the junction points of the gel networks are composed of crystallites. The gels can exhibit considerable turbidity in appearance, which is due to the formation of many small crystallites.

Fig. 2 shows a photomicrograph of UHMWPE/camphene gel as viewed in a cross-polarized light field. This figure reveals that crystallization has occurred in the gel. The white parts in the micrograph are crystallites.

In the spinning stage, the highly viscous UHMWPE solution is pumped through a nozzle to form a liquid filament that is subsequently quenched in a cooling bath. An as-spun fibre with an opaque appearance is thereby generated, containing almost all of the solvent. In this study, wide-angle X-ray diffraction (WAXD) was performed to elucidate the features of the as-spun fibre. Two WAXD patterns of the as-spun fibre are shown in Fig. 3. In Fig. 3a, the diffraction pattern is seen to display one broad halo in which the dim halo is due to the solvent (in the camphene system). Fig. 3b shows the WAXD pattern of extracted as-spun fibre in which a slight preorientation is generated during the solution spinning and quenching step. The diffraction pattern reflects some weak, but rather sharp reflections. These reflections are recognized as the (1 1 0), (2 0 0) and (0 2 0) planes of the orthorhombic crystal sturcture of polyethylene at the angles of 21.5°, 24.2° and 36.4°, respectively [13].

The viscosity of UHMWPE solution is infinite in the gel state. When the gelation temperature T_{gel}, is lowered, the viscosity of the polymer solution

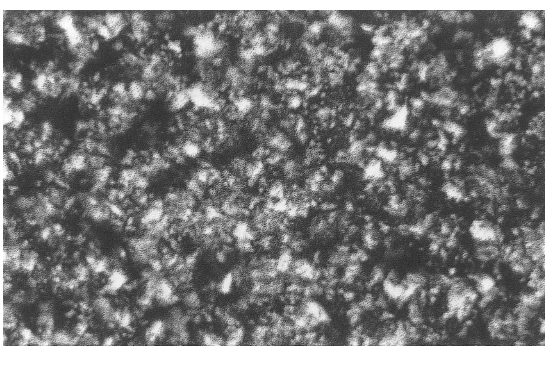

Figure 2 Photograph of crystallites in a gel taken using a polarizing microscope with crossed nickels, x 250.

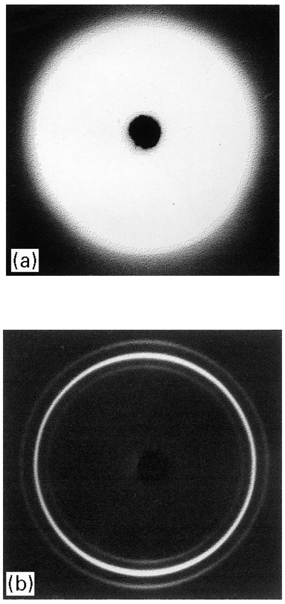

Figure 3 WAXD-patterns of UHMWPE: (a) gel in the camphene system, (b) an extracted as-spun fibre.

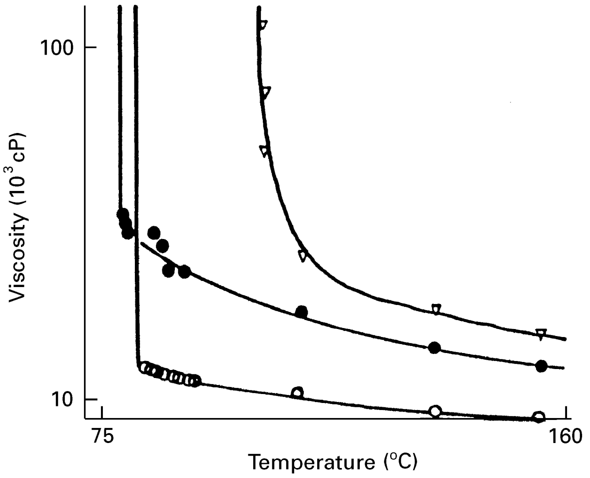

Figure 4 Effect of various solvents on gelation temperature of UHMWPE solutions; (○) camphene, (●) decalin, (▽) paraffin oil.

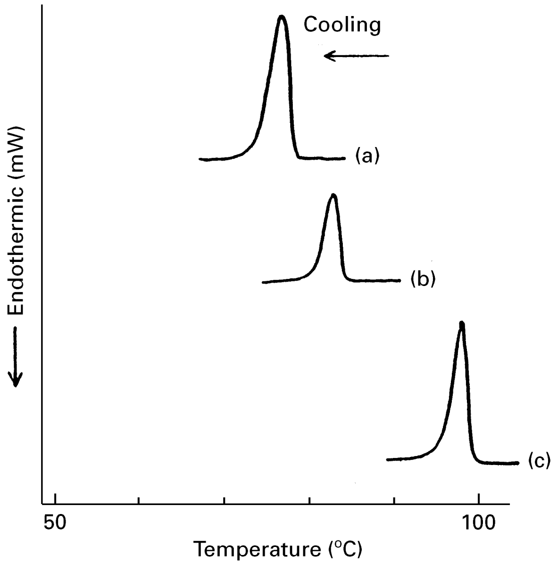

Figure 5 Gelation thermograms of UHMWPE solution in various solvents, cooling rate 5 °C min^{-1}; (a) decalin, (b) camphene, (c) paraffin oil.

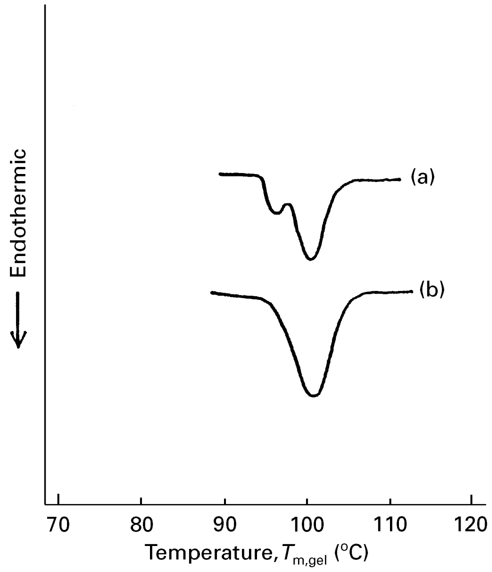

Figure 6 Gel melting temperature of UHMWPE gel for the camphene system (polymer concentration $C = 4$ wt %), heating rate 5 °C min^{-1}; dissolution time: (a) 2 h, (b) 5 h.

increases to an infinite value. This behaviour is due to UHMWPE molecules forming a crystal structure in the cooling process. Fig. 4 reveals that T_{gel} of the decalin, paraffin oil and camphene systems are 76.6 °C, 102.5 °C and 82.2 °C, respectively. The paraffin oil system has a significantly higher T_{gel} and is therefore less desirable than the other two systems from a processing point of view.

The DSC cooling curves for the gels are shown in Fig. 5. Single exothermic peaks appear at the recrystallization temperature, T_c. The fact that T_c is close to T_{gel} indicates that the gel formation is most likely caused by crystallization. When crystallization has occurred, the viscosity of the system increases rapidly. Conversion of a polymer solution to a gel causes the formation of a molecular network with junction points in the gel. The crystallites function acts as junction points in the gelation and the viscosity becomes infinite, which is characteristic of a gel.

Examples of DSC heating curves obtained from 4 wt % UHMWPE/camphene gel are shown in Fig. 6.

Two endothermic peaks are observed after 2 h dissolution, as observed in curve a. Such an appearance of two endothermic peaks is a unique feature of the gel in this study, suggesting that two melting processes are likely caused by the melting of two kinds of crystalline components existing in the present gel. The first curve is related to the melting of miniscale crystallites which could not crystallize sufficiently. The second curve is concerned with the melting of somewhat larger crystallites. However only a single endothermic peak appears in the gel after 5 h dissolution as observed in Fig. 6, curve b. The gel melting temperature, $T_{m,gel}$, is located around 101.2 °C. In this case, the small crystallites of the gel might have disappeared with increasing dissolution time. The polymer is more homogeneous after 5 h dissolution.

The heat of fusion (gelation enthalpy) of the gel is determined from the area of the endothermic curve. A comparison of the area of curves a and b reveals that the heat of fusion of the latter is more than the former. This implies that the degree of crystallinity of the latter is more than the former. Fig. 7 shows the dependence of $T_{m,gel}$ on the polymer concentration for the gels in various solvent systems. The $T_{m,gel}$ shifts to a higher temperature with an increase in the polymer concentration. According to Eldridge and Ferry [28], the dependence of $T_{m,gel}$ on the polymer concentration, C, is given by

$$\ln C = \Delta H / R T_{m,gel} + K \qquad (1)$$

where C is in g l^{-1}, ΔH is the enthalpy change of junction point, R is the gas constant and K is a constant. The relationship is derived by assuming that (a) two moles of cross-linking loci combine to form one mole of cross-linkage making a network, and (b) that the rates of formation and decomposition of cross-links are equilibrated.

The reciprocal of $T_{m,gel}$ for various solvent systems is plotted in Fig. 8 as a function of logarithmic polymer concentration. Linear relations are obtained for all gels. ΔH, which is determined from the slopes in Fig. 8, is 12, 24 and 46 kj mol^{-1} for decalin, camphene and paraffin oil systems, respectively. Values of ΔH for various solvent systems, as determined from Equation 1, are summarized in Table I. Because a UHMWPE is a crystalline polymer, no such single cross-links are formed by binary associations between polymer chains as assumed by Eldridge and Ferry. Instead, multiple cross-links formed by many small crystallites should exist in a UHMWPE gel, in addition to lamellae or spherulites. The fringed micellar crystallites form a network in the UHMWPE gel and behave as cross-linking junctions. According to Tan *et al.* [29], the ΔH of the chlorinated polyethylene–toluene system is also due to the formation of a precursor of a fringed micellar junction.

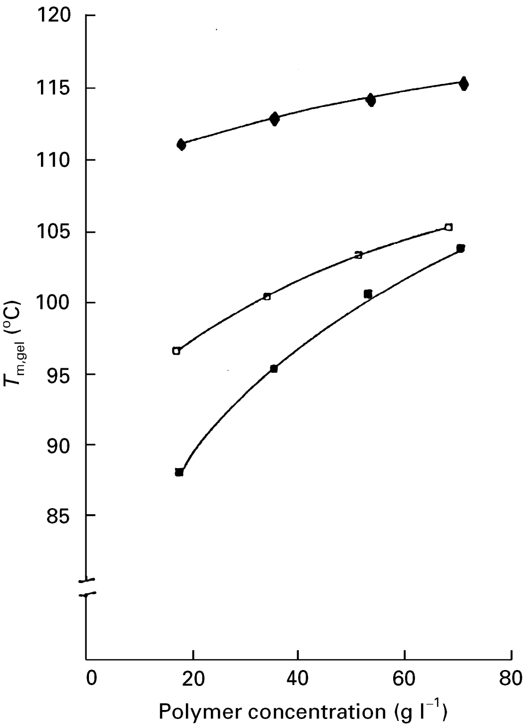

Figure 7 Dependence of the gel melting temperature on polymer concentration for (■) decalin, (◆) paraffin oil, (□) camphene, $\bar{M}_w = 1.5 \times 10^6$.

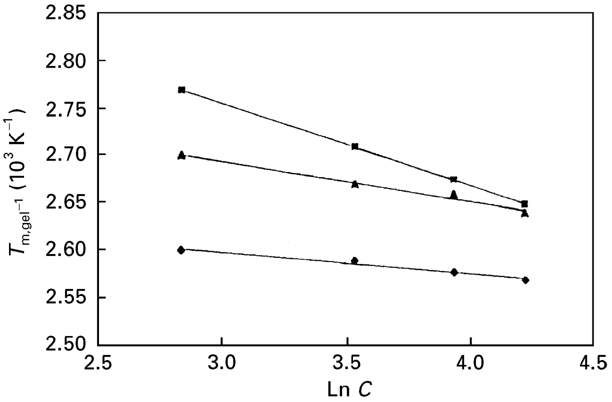

Figure 8 Dependence of the reciprocal of gel melting temperature on ln concentration. (■) decalin, (◆) paraffin oil, (▲) camphene.

TABLE I Gelation enthalpy of PE gel in various solvents estimated from the Eldridge–Ferry equation

Polymer–solvent	H(kJ mol^{-1})
Chlorinated PE–toulene	50–420 [29]
UHMWPE–decalin	12
UHMWPE–camphene	24
UHMWPE–paraffin oil	46

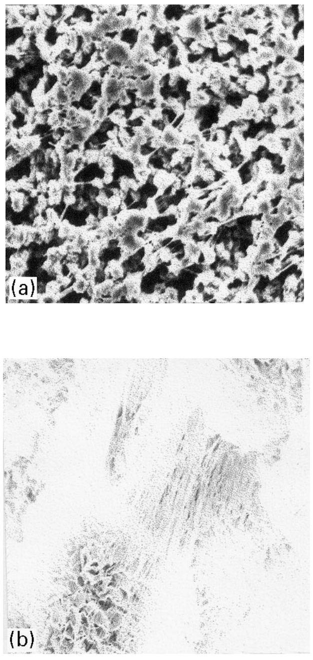

Figure 9 Scanning electron micrographs of an extracted as-spun fibre; (a) × 100, (b) × 1000.

A scanning electron micrograph of an extracted and undrawn as-spun fibre is shown in Fig. 9. This figure indicates that the cross-sectional shape of the fibre is

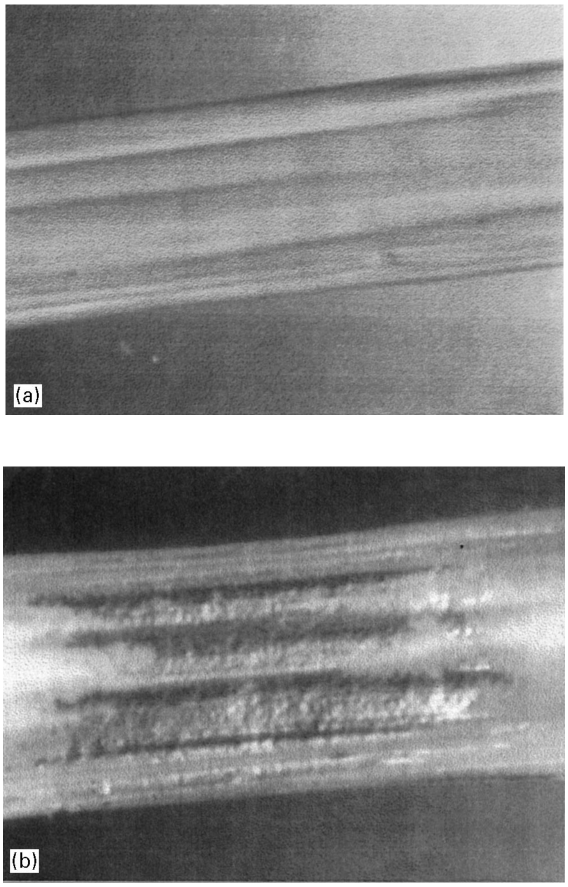

Figure 10 Scanning electron micrographs of a UHMWPE fibre drawn ten times, with (a) a smooth surface, and (b) an etched surface.

porous. The cause of the porosity may be attributed to the fact that the solvent of the wet as-spun fibre is extracted and volatilized, which might have resulted in the porous structure as found in Fig. 9a. At a higher magnification (Fig. 9b), a preorientation phenomenon is discerned in the fibrillar nature. This phenomenon indicates that the soft segment polyethylene can be drawn easily.

The scanning electron micrographs in Fig. 10 show UHMWPE fibre with a draw ratio of 10. Fig. 10a reveals that the surface of the fibre is rather uniform and smooth, as well as having a fibrillar nature. The striations in the highly drawn fibre are clearly observed. These striations are typical of a highly oriented polyethylene fibre. As indicated in Fig. 10b, the fibre surface has an etched structure. A possible reason is that the highly viscous polymer solution was not homogeneous during the mixing stage. It is therefore a form of defect in the UHMWPE fibre. Such structured defects should be avoided if possible, because the subsequent processing of the fibre can be greatly affected.

4. Conclusion

Results obtained in this study demonstrate that the gelation of UHMWPE from solution can be attributed to polymer crystallization. The gel crystal melts upon heating. Thus, the formation of a gel of UHMWPE becomes thermoreversible. T_c is in the vicinity of T_{gel}. The formation of a gel is well known to be caused by crystallization. T_{gel} of UHMWPE in paraffin oil is higher than in the other solvents, which makes paraffin oil a less desirable sovlent for processing. On the other hand, the lower viscosity of the camphene system is favoured for gel spinning, from the perspectives of mixing and chain disentanglement. $T_{m,gel}$ depends on the polymer concentration and increases with increasing polymer concentration. The polymer concentration of $T_{m,gel}$ can be accurately represented by the Eldridge–Ferry type of plot.

References

1. A. J. PENNINGS and J. C. TORFS, *Coll. Polym. Sci.* **257** (1979) 547.
2. P. SMITH and P. J. LEMSTRA, *J. Mater. Sci.* **15** (1980) 505.
3. P. SMITH, P. J. LEMSTRA and H. C. BOOIJ, *J. Polym. Sci. Polym. Phys. Ed.* **19** (1981) 877.
4. P. SMITH and P. J. LEMSTRA, DSM US Pat. 4344 908 (1982).
5. P. SMITH, P. J. LEMSTRA, R. KIRSCHBAUM and J. P. L. PIJPERS, DSM, Eur. Pat. 0077 590A1 (1982).
6. P. SMITH, P. J. LEMSTRA, R. KIRSCHBAUM and J. P. L. PIJPERS, DSM US Pat. 4436 689 (1984).
7. S. KAVESH and D. C. PREVORSEK, Allied Signal, Eur. Pat. 0064 167A1 (1982).
8. S. KAVESH and D. C. PREVORSEK, Allied Signal, US Pat. 4413 110 (1983).
9. M. MOTOOKA, H. MANTOKU and T. OHNO, Eur. Pat. 0115 192 A2 (1983).
10. T. SHIRAKI, Y. YOSHIMURA and K. NAKASHIMA, Eur. Pat. 0190 878 A2 (1986).
11. A. E. ZACHARIADES and J. A. LOGAN, *J. Polym. Sci. Polym. Phys. Ed.* **21** (1983) 821.
12. M. MATSUO and C. SAWATARI, *Macromolecules* **19** (1986) 2028.
13. R. C. DOMSZY, R. ALAMO, C. O. EDWARDS and L. MANDELKERN, *ibid.* **19** (1986) 310.
14. H. MATSUDA, T. INOUE, M. OKABE and T. UKAJI, *Polymer J.* **19** (1987) 323.
15. M. MATSUO, C. SAWATARI, M. IIDA and M. YOUEDA, *ibid.* **17** (1985) 1197.
16. H. PHUONG - NGUYEN and G. DELMAS, *Macromol* **25** (1992) 414.
17. T. KYU, K. FUJITA, M. H. CHO and T. KIKUTANI, *ibid.* **22** (1989) 2238.
18. A. J. McHUGH, W. R. BURGHARDT and D. A. HOLLAND, *Polymer* **27** (1986) 1585.
19. P. SWITH, H. D. CHANZY and B. P. ROTZINGER, *J. Mater. Sci* **22** (1987) 523.
20. T. OKUMARA and M. MATZUO, *Polymer J.* **18** (1986) 741.
21. P. J. BARHAM, *Phys. Technol.* **17** (1986) 167.
22. P. J. LENSTRA, N. A. J. M. VAN AERLE and C. W. BASTIAANSEN,. *Polymer J*, **19** (1987) 85.
23. V. G. KULICHIKHIN *et al. Vysokomol. Soyed.* **A32** (1990) 77.
24. A. ZHANG, Z. WU, K. CHEN and P. LU, *J. Appl. Polym. Sci.* **38** (1989) 1369.
25. K. CHEN, A. ZHANG, P. LU and Z. WU, *ibid.* **38** (1989) 1377.
26. W. L. CHEN, D. M. LEE, L. T. CHEN and M. T. YEH, US Pat. 5342 567 (1994).
27. A. TAKAHASHI, T. NAKAMURA and I. KAGAWA, *Polym. J.* **3** (1972) 207.
28. J. E. ELDRIDGE and J. D. FERRY, *J. Phys. Chem.* **58** (1954) 992.
29. H. TAN, B. H. CHANG, E. BEAR and A. HILTNER, *Eur. Polym. J.* **19** (1983) 1021.

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