Macromol. Symp. ***152,*** *15–27 (2000)*

Rheology of metallocene catalysed polyethylenes: Energy consumption perspective

Anton Santamaría* [a], Juan Francisco Vega[a], Antonio Muñoz-Escalona[b], Pilar Lafuente[b]

[a] Department of Polymer Science and Technology,
University of the Basque Country,
P.O. Box 1072, 20080 San Sebastián, Spain. e-mail: popsaiba@sq.ehu.es

[b]Repsol Investigación y Desarrollo, C/ Embajadores 183, 28043, Madrid, Spain

SUMMARY: The rheological properties of a large series of metallocene catalysed polyethylenes, obtained via metallocene single site catalysts (SCC) have been analysed. A detailed analysis of the effect of frequency and temperature on dynamic viscoelastic functions reveals that very low amounts of long chain branching (less than one per chain) can be detected by rheological methods. The effect of this molecular parameter, as well as the effect of molecular weight, polydispersity and short chain branching content on extrusion rheometry results are investigated, showing some possible routes to improve the processability of metallocene catalysed polyethylenes, and to lessen the time and energy consumption during processing.

Introduction

Recent advances in catalysts technology have lead to the development of metallocene catalysts systems, that have been regarded as the future trend in polyolefin polymerisation[1-7]. Polyolefins obtained from such technology are characterised by a controlled molecular structure or architecture: the main features of these materials are the narrow molecular weight distribution (M_w/M_n=2-3) and the homogeneous distribution of short chain branching (SCB) along the polymer main chain. These special characteristics cause a great improvement in physical and mechanical attributes when compared with polyolefins made from standard Ziegler-Natta technology: low density and melting temperature, and better optics, strength and toughness. However, the disadvantages of these polymers are their poor processability due to their low shear sensivity and low melt tension, and the requirement of more time and energy when are processed. A comparison of blown film processability energy consumption of conventional and metallocene catalysed polyethylenes has been presented by Garavilla[8]. However, these catalyst systems allow a good control on their

CCC 1022-1360/00/$ 17.50+.50/0

molecular design and have lead to the development of specific compounds able to produce polymers with "taylor-made" properties: good physical and mechanical properties and the unique advantage of easy processability[9-15]. Two ways are possible to obtain these materials: the generation of multimodal samples, either by mixing two or more metallocene catalysts of different activity[16] or by one "specially designed" metallocene catalyst[17]; and the incorporation of long chain branches (LCB) during polymerisation maintaining the polydispersity index[18-24].

Nowadays it is accepted that metallocene catalysts, in certain conditions, can produce vinyl terminated chains, that is to say macromonomers with the ability of incorporate into the growing chain giving rise to long chain side structures in the polymer main chain[18-24]. The nature of these structures is different in conventional and metallocene catalysed materials. In conventional PE-s the number of LCB is moderate or high (more than one long branch per macromolecule); in metallocene catalysed polymers the number of branches in less than one per macromolecule and the materials could be treated as blends of linear and branched species.

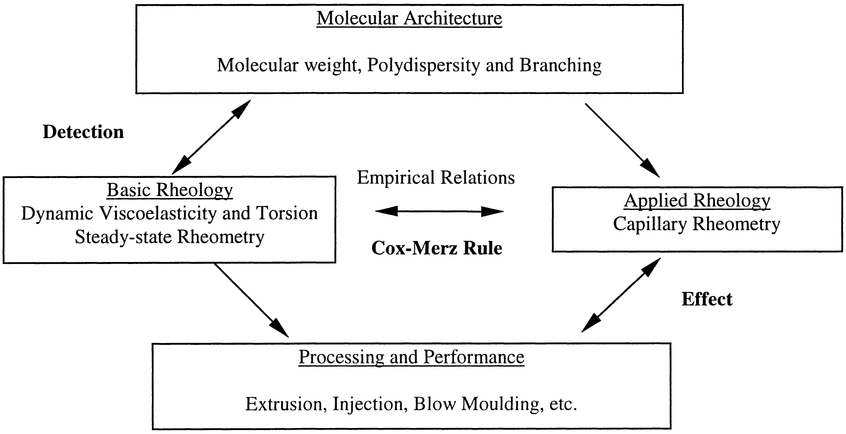


Fig. 1: Relation between Basic Rheology and Applied Rheology in order to determine the presence of LCB in metallocene PE-s and its effect on processing

The low LCB content in metallocene resins is very difficult to measure by analytical methods, but rheological techniques can be a convenient tool to detect the presence of these structures$^{25)}$. Long chain branching in PE-s, even at low levels, causes a great effect on polymer rheology. Linear viscoelastic measurements at low frequencies and torsion steady-state measurements at low shear rates are two common experimental techniques that can be used to detect the presence of these structures. The effect of LCB on processing can be estimated using melt capillary rheometry techniques (see Fig. 1).

Experimental

Materials

The rheological properties of a series polyethylenes, supplied by Repsol Química S.A.. (Madrid), have been analysed. Unimodal homopolymers and copolymers ethylene/1-hexene were obtained via metallocene single site catalyst following the method of Kaminsky and co-workers$^{26)}$. The molecular weight of the materials ranges from 14 000 to 320 000 and polydispersity index from 1.8 to 3.5 LCB content is also variable, between 0 and 50 branches C_4 /1000 C. As reference samples, conventional polydisperse HDPE-s and LLDPE-s in the same range of molecular weight have been tested.

Rheometry

Dynamic torsion measurements in the linear regime and steady-state torsion measurements have been carried out in a viscoelastometer CARRIMED CSL-100 between 0.001 and 100 rad/s or s^{-1}, and the temperature range 130-205°C, using a parallel plates geometry, in order to determine the characteristics dynamic viscoelastic functions $G'(\omega)$, $G''(\omega)$, $\eta'(\omega)$ and $\eta^*(\omega)$ and the steady-state viscosity, $\eta(\dot{\gamma})$. Experiments in a capillary rheometer Sieglaff-McKelvey (Tinius Olsen) between 1 and 100 s^{-1} and a temperature range 145-190°C have been performed. This technique allowed us to obtain the flow curves and extrudates of some of the materials studied. The surface of these extrudates has been observed by scanning electron microscopy in a HITACHI-2100 microscope.

Results and discussion

The effect of the presence of low amounts of long chain branching on rheological behaviour of metallocene polyethylene has been the scope of several publications[11-15,25]. The principal features of slightly long chain branched polymers can be resumed as follows[27-36]:

a) higher Newtonian viscosities and relaxation times (defined as the inverse of the frequency for the onset of non Newtonian behaviour); b) a more pseudoplastic behaviour; c) higher melt elasticity and d) higher activation energies of flow, than those presented by linear materials of similar molecular weight, molecular weight distribution and short chain branching (comonomer) content.

Newtonian viscosity versus molecular weight (Fig. 2) and versus relaxation time (Fig. 3) plots allow us to determine what material is suspect of contain long branches. Linear polymers of narrow MWD fit to power laws in both figures: the polymers with long chain branches do no fit to these equations. It is necessary to point out that the effect of polydispersity and LCB in Fig. 3 is the same. Neither of the linear polydisperse conventional polymers fit to η_o-τ_o correlation, even though fit in an acceptable manner to η_o-M_w power law.

The work of Bersted[28] on polyethylenes leads to the conclusion that the presence of very low amounts of LCB give rise to spectacular variations in rheological properties, due to changes of the relative proportions of branched and linear species with branch concentration. This author proposes a model which explains the viscosity maximum observed at low content of LCB.

Fig. 4 shows the frequency dependence of elastic and viscous moduli for selected polymers (M_w=130 000 and M_w/M_n=3). Material suspect of contain LCB present a more elastic character than the corresponding to linear conventional LLDPE. The relative value of elastic modulus, G', over the viscous modulus, G", at low frequencies yields an elastic index that describes, in linear polymers, the MWD[36,37]. In polydisperse and in branched materials the crossover of G' and G" moves to lower frequencies as compared to linear polymers.

The higher melt elasticity found in some of the metallocene polymer studied suggests the presence of a network structure produced by the entanglements as a result of the presence of long chain branches.

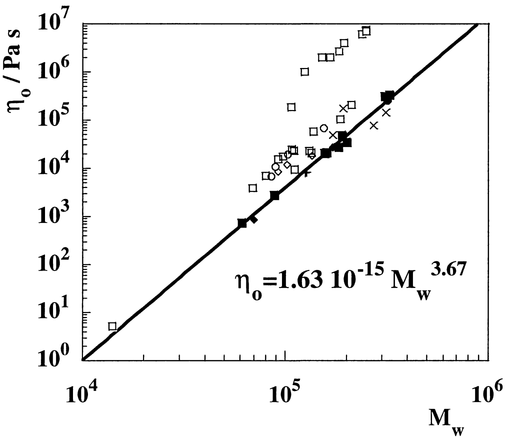


Figure 2

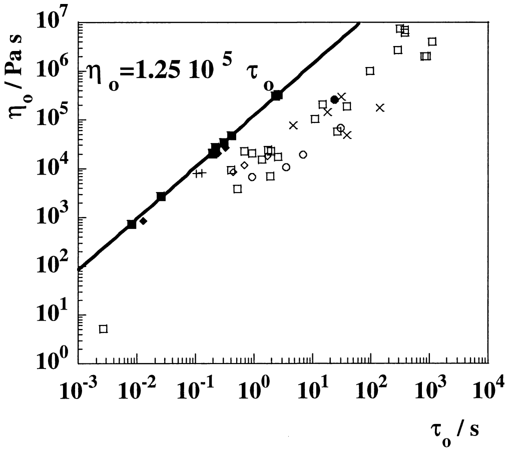


Figure 3

Fig. 2 and Fig. 3: Newtonian viscosity versus weight average molecular weight and relaxation time at 190°C for the investigated materials. Black symbols: linear metallocene PE-s; white symbols: metallocene PE-s suspect of contain long branches; (+x) conventional polydisperse PE-s. The solid line represents the power law followed by linear materials in the figures

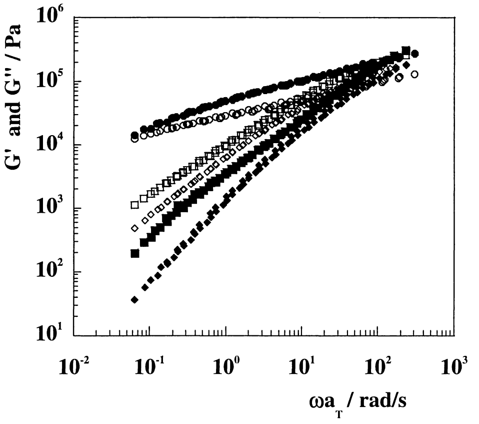


Fig. 4: Time-temperature superposition of storage (black symbols) and loss (white symbols) moduli for selected polymers of M_w=130 000 and M_w/M_n=3 at T_R=190°C. Circles (conventional LLDPE); squares (metallocene copolymer P162) and diamonds (metallocene copolymer P109)

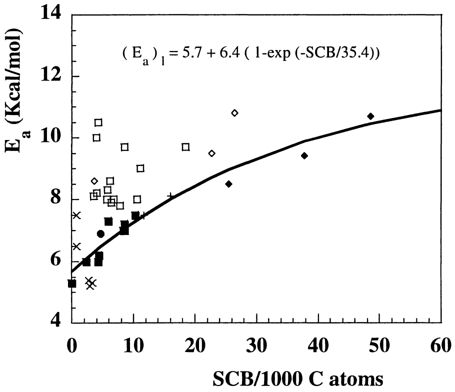


Fig.5: Activation energy values versus SCB content for metallocene copolymers (black and white symbols) and conventional PE-s (+x). The solid line represents the fit of linear polymers data to the equation given in the figure

The application of the time-temperature superposition to the viscoelastic data showed that linear PE-s have values of activation energy of flow, E_a, dependent on SCB content, and that long branched PE-s posses higher E_a values than one would expect taking into account their SCB content (see Fig. 5).This result is consistent with the accepted idea that long branching increases the values of this parameter: in conventional LDPE the activation energy reaches a value of 18 kcal/mol[38)]. In a recent paper[25)] it has been pointed out that it is possible to determine the level of LCB by means of the values of E_a (an independent parameter of MW and MWD) if the content of SCB due to the comonomer is known:

$$LCB / 1000C = 0.0176\left[(E_a)_l - (E_a)_b\right] \qquad (1)$$

where $(E_a)_l$ is the activation energy of flow of a linear polymer with the same SCB content that the branched polymer of activation energy $(E_a)_b$. Equation 1 has been estimated from the results obtained by Hughes for conventional PE-s in which long chain branching was introduced by peroxide addition[27)]. The values of LCB content have been calculated for metallocene catalysed polymers of M_w=130 000 and M_w/M_n=3. The values are listed in Tab. 1

Tab. 1. LCB level in selected polymer (M_w=130 000 and M_w/M_n=3)

Material	F2	P162	P109	XV	BP58
LCB /1000 C atoms	0	0.015	0.032	0.040	0.060

The application of the Cox-Merz rule[39)] for these materials is presented in Fig. 6. This rule predicts that the magnitude of the complex viscosity in dynamic experiments and the viscosity in steady-state measurements is the same. The Cox-Merz rule is fulfilled very well by the materials studied, and points out that dynamic measurements can predict the behaviour of the polymer at characteristic shear rate values of polymer processing. Fig. 6 also shows that the pseudoplastic character of branched polymers is more pronounced than the corresponding to linear material, giving rise to lower viscosities at high shear rates: this results in less time and energy consumption during processing.

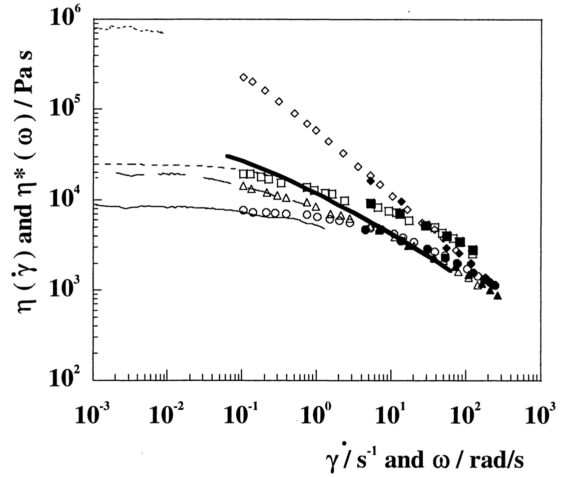


Fig. 6: Cox-Merz rule for selected polymers (M_w=130 000 and M_w/M_n=3) at 190°C. Thin lines: steady state measurements in torsion; white symbols: dynamic measurements in torsion; and black symbols: steady-state measurements in capillary extrusion. Circles (conventional LLDPE F2), squares (metallocene copolymer P162); diamonds (metallocene copolymer P109), triangles (commercial metallocene copolymer XV). Thick line corresponds to dynamic results of metallocene copolymer BP58 (with the highest LCB content, 0.06 branches /1000 C atoms)

In Fig. 7 we can observe the effect of MW in the flow curve of selected linear metallocene polymers. An increase in MW causes an increase on the applied shear stress, and thus in the energy consumption. A series of instabilities appear in these polymers during the flow. The first instability starts at a critical value of the shear stress of 0.18 MPa[40-46)]. The rheology of the polymer is steady in this regime, that is to say, apparently the shear stress does not change with time at a given shear rate, but the extrudates show a superficial irregularity or distortion called "sharkskin", which is typical in polyolefins of high MW and narrow MWD. The microphotographs obtained by SEM for the extrudates in this regime at a constant value of shear stress of 0.20 MPa can be observed in Fig. 8. A second unsteady flow takes place when the shear stress reach a value of =0.30-0.40 MPa[40,42-44,47-50)]. In this case the rheology is chaotic: the shear stress value at a given shear rate varies between a maximum and a minimum and the extrudate shows a “bamboo-like” irregularity. It seems that both distortion regimes are caused by an adhesive failure in melt-metal interface.

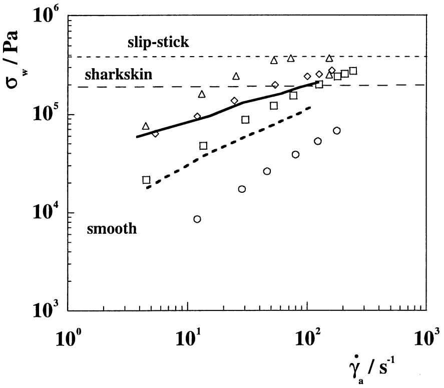
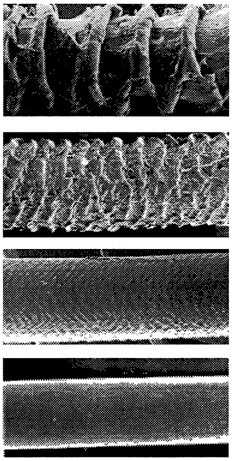


Fig. 7: Effect of MW on flow curves at 190°C for selected polymers (M_w/M_n=3). Circles (linear metallocene P148), squares (conventional LLDPE F2), diamonds (linear metallocene P150) and triangles (linear metallocene PCWSB13). Lines (conventional polydisperse PE-s)



a) PCVSB13
M_w=200 000

b) P150
M_w=157 500

c) F2
M_w=125 00

d) P148
M_w=70 300

Fig. 8: Photographs obtained by SEM for extrudates of the linear polymers in Fig. 9 in the sharkskin regime (except for low MW material P148)

Fig. 9 shows the effect of the presence of LCB in the flow curves of metallocene based polymer of the same MW and MWD. It can be seen in the figure that very low branched material (P162) shows higher values of the shear stress in the shear rate range studied, so as the critical shear rate for the onset of “sharkskin” regime decreases with respect to the linear polymer. As LCB level increases the onset of the distortion is shifted to lower values of shear rate (P109). However, it seems that for the XV sample the content of LCB is enough high to cause a decrease in shear stress values in all shear rate range, and the critical shear stress for the onset or the distortions is not reached. It has not been possible to obtain extrusion data for BP58 polymer (that possesses a LCB content of 0.06 branches / 1000 C atoms) due to the lack of material, but the simulation of the flow curve applying the Cox-Merz rule points out that the material would flow in a similar manner to XV polymer. In Fig. 10 we can observe the microphotographs obtained by SEM for the materials represented in Fig. 9. Although a very low value in the content of LCB produces an increase in the time and energy consumption for processing the polymers and a worsening in the appearance of the extrudates, for moderate and high values of LCB the shear stress diminishes and the processability improves with respect to that corresponding to linear conventional materials, as can be predicted from Bersted model[28].

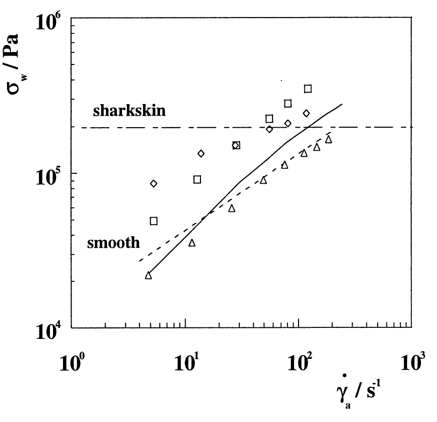
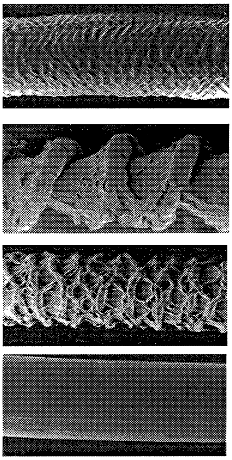


Fig. 9: Effect of LCB on flow curves at 190°C for selected polymers (M_w=130 000 and M_w/M_n=3). Solid line (linear conventional LLDPE F2), squares (metallocene copolymer P162), diamonds (metallocene copolymer P109) and triangles (commercial metallocene copolymer XV). Dashed line represents the Cox-Merz simulation of the flow curve for BP58 metallocene copolymer (thick line in Fig. 6)


a) F2
0 LCB/1000 C

b) P162
0.015 LCB/1000 C

c) P109
0.032 LCB/1000 C

d) XV
0.040 LCB/1000 C

Fig. 10: Photographs obtained by SEM for extrudates of the linear polymers in Fig. 9 in the sharkskin regime

For one of the linear metallocene polyethylenes studied (M_w=160 000, M_w/M_n=3 and SCB/1000C=8) an anomalous behaviour has been observed in extrusion at low temperatures. For the lowest temperature studied (145°C) this polymer did not show the characteristic sharkskin regime, even though the critical value of shear stress (0.18 MPa) was reached. For 160, 175 and 190°C the distortion appeared and its magnitude diminished with temperature, as it can be observed in Fig. 11, a photograph of the extrudates obtained at different temperatures in the sharkskin regime at 0.20 MPa.

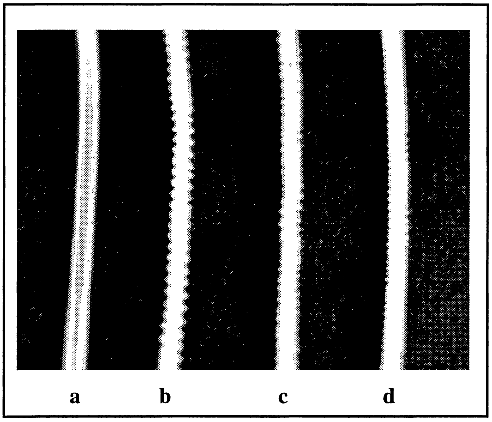


Fig. 11: Photograph of linear metallocene copolymer (M_w=160 000 and M_w/M_n=3) extrudates obtained in the sharkskin regime (0.20 MPa) at different temperatures:
a) 145°C (processability window), b) 160°C, c) 175°C and d) 190°C

This anomaly had not been observed by the moment for metallocene polymers. Keller and co-workers[51-55)] found a "temperature window" between 148-152°C for high MW conventional polyethylenes in which surface roughness was absent. These authors suggested the emergence of a new, flow-induced mesophase near the capillary wall, consistent with the hexagonal crystal form of polyethylene[54)]. The observation and the study of this "temperature window" is of great interest in polyolefin processing, since supposes lower processing pressures and temperatures, this is the energy consumption, with improved processability.

Conclusions

Metallocene catalysts can give rise to long chain side structures in the polymer main chain. To the difference of conventional polyethylenes, in metallocene catalysed polymers the number of branches is very small (typically less than one per molecule).

Rheological techniques are useful to detect the presence of such a small content of LCB and to analyse the effect of its presence in the processing conditions.

Acknowledgements

The authors wish to thank Repsol Química for permission to publish this work. Financial support through CICYT (MAT 96-0477) and UPV/EHU (UPV 203.215-EB 172/95) is acknowledged. J.F.V. thanks the Government of the Basque Country for a research fellowship.

References

(1) T. Sasaki, T. Ebara, H. Johoji, *Polym. Adv. Technol.* **4,** 406 (1993)

(2) A. Guyot, L. Böhm, T. Sasaki, U. Zucchini, F. Karol, Y. Hattori, *Makromol. Chem., Macromol. Symp.* **66**. 311 (1993)

(3) F. Garbassi, L. Gila, A. Proto, *Polymer News* **19**, 367 (1994)

(4) A. Batistini, *Macromol. Symp.* **100**, 137 (1995)

(5) A. Díaz Barrios, R. Mendez, Y. Becker, P. Joskowicz, J.C. Perfetti, *Latin Am. Appl. Res.* **26**, 49 (1996)

(6) K. Soga, *Macromol. Symp.* **101**, 281 (1996)

(7) A. Todo, N. Kashiwa, *Macromol. Symp.* **101**, 301 (1996)

(8) Y. R. de Garavilla, *Tappi Journal* 78 (**6**), 191 (1995)

(9) G.W. Knight, S. Lai, Procc. VIII Int. Polyolefins Conf., *SPE RETEC* **226** (1993)

(10) S. Lai, G.W. Knight, *ANTEC'93*, 1188 (1993)

(11) B.A. Story, G.W. Knight, *MetCon'93* 111 (1993)

(12) S. Lai, T.A. Plumbey, T.I Butler, G.W. Knight, C.I. Kao, *ANTEC'94* 1814 (1994)

(13) Y.S. Kim, C.I. Chung, S.Y. Lai, K.S. Hyun, *ANTEC'95* 1122 (1995)

(14) Y.S. Kim, C.I. Chung, S.Y. Lai, K.S. Hyun, *Korean J. Chem. Eng.* **13**, 194 (1996)

(15) Y.S. Kim, C.I. Chung, S.Y. Lai, K.S. Hyun, *J. Appl. Polym. Sci.* **59**, 125 (1996)

(16) J.A Ewen, H.C. Welborn, Exxon Chemicals, EP 0128045

(17) W. Michiels, A. Muñoz-Escalona, Repsol S.A., EP 0719797

(18) A. S. Mehta, C.S. Speed, J.A.N. Canich, N. Baron, B.J. Folie, M. Sugawara, A. Watanabe, H.C. Welborn, Exxon Chemicals, IP WO 96/12744

(19) S.Y. Lai, J.R. Wilson, G.W. Knight, J.C. Stevens, P.W.S. Chum, Dow Chemical Company, US Patent 5, 272, 236

(20) P. Howard, P.J. Maddox, S.R. Partington, BP Chemicals Ltd., EP 0676421A1
(21) M. Sugawara, *SPO'94* 39 (1994).
(22) A.E. Hamielec, J.B.P. Soares, *SPO'96* 95 (1996)
(23) A.E Hamielec, J.B.P. Soares, *Prog. Polym. Sci.* **21**, 651 (1996)
(24) D. Beigzadeh, J.B.P. Soares, A. Hamielec, *Polym. Reaction Eng.* **5**, 141 (1997)
(25) J.F. Vega, A. Santamaría, A. Muñoz-Escalona, *Macromolecules* **31**, 3639 (1998)
(26) W. Kaminsky, H. Hahnsen, K. Külper, R. Wöldt, US Patent 4, 542, 199
(27) J.K. Hughes, *SPE Antec Tech. Papers* **29**, 306 (1983)
(28) B.H. Bersted, *J. Appl. Polym. Sci.* **30**, 3751 (1985)
(29) B.D. Dickie, R.J. Koopmans, *J. Polym. Sci.: Part C: Polym. Letters* **28**, 193 (1990)
(30) K.J. Kim, B.K. Kim, *J. Appl. Polym. Sci.* **48**, 981 (1993)
(31) H. Mavridis, R. Shroff, *J. Appl. Polym. Sci.* **49**, 299 (1993)
(32) R.K. Chonan, *J. Appl. Polym. Sci.* **54**, 487 (1994)
(33) A. Harlin, E.-L. Heino, *J. Polym. Sci.; Part B: Polym. Phys.* **33**, 479 (1995)
(34) M.G. Lachtermacher, A. Rudin, J. *Appl. Polym. Sci.* **58**, 2433 (1995)
(35) R. Shroff, H. Mavridis, *J. Appl. Polym. Sci.* **57**. 1605 (1995)
(36) R. Shroff, A. Prasad, C. Lee, *J. Polym. Sci.: Part B: Polym. Phys.* **34**, 2317 (1996)
(37) E. R. Harrel, N. Nakajima, *J. Appl. Polym. Sci.* **29**, 995 (1984)
(38) H. Mavridis, R.N. Shroff, *Polym. Eng. Sci.* **32**, 1778 (1992)
(39) W.P. Cox, E.H. Merz, *J. Polym. Sci.* **28**, 619 (1958)
(40) L.A. Utracki, R. Gendron, *J. Rheol.* **28**, 101 (1984)
(41) Y.H. Lin, *J. Rheol.* **29**, 605 (1985)
(42) A.V. Ramamurthy, *J. Rheol.* **30**, 337 (1986)
(43) D.S. Kalika, M.M. Denn, *J. Rheol.* **31**, 815 (1987)
(44) N. El Kissi, J.M. Piau, *J. Rheol.* **38**, 1447 (1994)
(45) S.Q. Wang, P.A. Drda, Y.W. Inn, *J. Rheol.* **40**, 875 (1996)
(46) S. Pudjijanto, M.M. Denn, *J. Rheol.* **38**, 1735 (1994)
(47) G.V. Vinogradov, A.Y. Malkin, Y.G. Yankovskii, E.K. Borisenkova, B.V. Yarlykov, G.V. Berezhnaya, *J. Polym. Sci.: Part A: Polym. Chem.* **10**, 1061 (1972)
(48) S.Q. Wang, P.A. Drda, *Macromolecules* **29**, 2827 (1996)
(49) S.Q. Wang, P.A. Drda, *Macromolecules* **29**, 4115 (1996)
(50) S.Q. Wang, P.A. Drda, *Rheol. Acta* **36**, 128 (1997)
(51) A.J. Waddon, H.H. Keller, *J. Polym. Sci.: Part B: Polym. Phys.* **28**, 1063 (1990)
(52) A.J. Waddon, H.H. Keller, *J. Polym. Sci.: Part B: Polym. Phys.* **30**, 923 (1992)
(53) J.W.H. Kolnaar y A. Keller, *Polymer* **35**, 3863 (1994)
(54) J.W.H. Kolnaar y A. Keller, *Polymer* **36**, 821 (1995)
(55) J.W.H. Kolnaar y A. Keller, *Polymer* **38**, 1817 (1997)