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Successive self-nucleation/annealing (SSA): A novel technique to study molecular segregation during crystallization

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Summary

A new procedure to fractionate ethylene/α-olefin copolymers using *DSC* is presented. This procedure allows melt/melt and melt/solid segregation to occur during thermal cycles that promote self-nucleation, crystallization and annealing processes (*Successive Self-Nucleation/Annealing*, SSA). The SSA has been compared with the *Step-Crystallization* (SC) method proposed earlier in the literature to qualitatively characterize chain branching distribution in a faster and easier way than *Temperature Rising Elution Fractionation* (*TREF*). In general, SSA produces better fractionation than SC and the *DSC* derived chain branching distribution by SSA can be qualitatively comparable to that obtained by *TREF*. The SSA technique could have important applications for the characterization of polymers that crystallize over a broad temperature range.

Introduction

The versatility in physical properties of ethylene/α-olefin copolymers depends on the type, amount and distribution of the α-olefin comonomer in the resin. The influence of the distribution of the α-olefin along the chain is particularly important (1-6), a fact intimately connected to the nature and type of the catalytic system employed during copolymerization of ethylene(6-9). Many of these copolymers can exhibit a highly heterogeneous comonomer distribution (CD) in the sense that the distribution of the short chain branches (SCB) is heterogeneous along one particular chain, and each chain or group of chains may possess a different chain branching distribution (8-14).

The particular interest to characterize the CD in Linear Low Density Polyethylenes (LLDPE, ethylene/α-olefin copolymers) led to the development of *Temperature Rising Elution Fractionation* (*TREF*). This technique produces separation by the elution of polymer fractions at successively rising temperatures of a material that has been allowed to crystallize from solution on an inert support during very slow cooling or multiple steps. Such slow crystallization from solution favors molecular segregation by short chain branching content and distribution with a limited influence of molecular weight (10). Even though the technique has been applied successfully, its implementation is difficult and expensive, and measurement times can be very long. If a rapid characterization of an ethylene/α-olefin copolymer is desired, then *TREF* might not be a practical option. This is why several authors have developed quicker and easier characterization methods using *Differential Scanning Calorimetry* (*DSC*); such methods involve *Step-Crystallization* (SC) from the melt based on the step crystallization from solution that is applied in the *TREF* technique. These SC methods

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can provide qualitative preliminary information on the CD of the polymer under study in less time and without any additional instrumentation than a conventional *DSC* (8,15,16).

In this work we have developed a new thermal treatment designed to produced better fractionation than SC. The *Successive Self-Nucleation/Annealing* (SSA) method is based on a superposition of self-nucleation and annealing cycles, where each cycle is similar to those designed by Fillon *et al.* (17) for the evaluation of the self-nucleation process in polypropylene (PP), a procedure used by our group in the past to study the fractionated crystallization of polyolefins dispersed in an immiscible matrix (18,19). We have applied SSA to several ethylene/α-olefin copolymers and compared its results with those obtained by SC methods and in one case with *TREF* results.

Experimental

Materials

The polymers used in this study were: a High-Density Polyethylene (HDPE) Altaven 7000F ethylene/1-butene copolymer with a bimodal distribution of molecular weights, manufactured by *Poliolefinas Industriales* (Venezuela); a Linear-Low Density Polyethylene synthesized by a solution process Dowlex D2045 ethylene/1-octene copolymer (LLDPE-o) of *Dow Chemical*; a Very Low-Density Polyethylene (VLDPE) Engage 8480 ethylene/1-octene copolymer manufactured by *DuPont Dow Elastomers* based on the Insite Technology (metallocene catalysts) and an Ultra Low-Density Polyethylene (ULDPE) Nuld2 ethylene/propene/1-butene copolymer of *Enichem Polimeri* (Italy), produced in a modified high pressure process using supported Ziegler-Natta (Z-N) catalysis. A blown film grade LLDPE-b ethylene/1-butene copolymer synthesized by a solution process, previously characterized via *TREF* was also evaluated (14). The characteristics of the copolymers are presented in Table 1.

Table 1. Basic characteristics of the materials used in this study.

Materials	MFI [dg/min]	Density [g/cm^3]	$\overline{M}_w$ and Polydispersity	SCB Content[1] [-CH$_3$/1000C]	T_c, T_m, X_c [2] [°C]/[°C]/[%]
HDPE Altaven 7000F	0.05	0.956	230,000/18.4	4.4	115/131/71
LLDPE-o Dowlex D2045	1.0	0.920	133,000/6.6	11.5	102/122/50
VLDPE Engage 8480	1.0	0.902	-	-	78/99/33
ULDPE Nuld2	1.3	0.875	-	88.0	86/107/19
LLDPE-b 1-butene	1.4	0.922	159,700/4.2	12.7	102/119/43

1: Short Chain Branching. 2: Peak crystallization and melt temperature (T_c, T_m) at 10°C/min and crystallinity (X_c) calculated by *DSC* heating scans at same rate.

Differential Scanning Calorimetry (DSC)

The neat polymers were compression molded at 170°C into 0.5 mm sheets. From these sheets small (10 mg) disc samples were cut. The samples were encapsulated in Aluminum pans and high purity dry Nitrogen was used as an inert atmosphere for all tests in a *Perkin Elmer DSC7*. For a previous characterization of thermal behavior of neat polymers, *DSC* cooling and heating curves were performed at 10°C/min after the samples were held in the melt at 170°C for 3 minutes in order to erase all previous thermal history. Then, with the purpose of evaluating the CD, two distinct *DSC* methods were employed, as follows:

1) *Step-Crystallization* (SC): First, the sample was melted at 170°C for 3 minutes. Then it was step crystallized by rapidly decreasing the temperature from the melt (at 60°C/min) to the crystallization temperature (T_c), where the first crystallization step was completed after 5 minutes at T_c. Then the temperature was again quickly decreased (at 60°C/min) to the next T_c and the process of isothermal crystallization was repeated for the same time, 5 min. Isothermal crystallization temperature stages were separated from each other by 5°C. In the present set of experiments the isothermal crystallization temperature range used was from 124 to 59°C, followed by cooling to 25°C (also at 60°C/min). Finally, the melting behavior of the step crystallized sample was recorded by performing a *DSC* heating scan at 10°C/min. The method is based on references 8,15 and 16.

2) *Successive Self-Nucleation/Annealing*, (SSA): The sample was melted at 170°C for 3 minutes. Then, it was cooled at 10°C/min to 25°C in order to create an initial "standard" thermal history. Subsequently, a heating scan at 10°C/min was performed up to a selected self-seeding and annealing temperature denoted T_S, where the sample was isothermally kept for 5 min before cooling it again at 10°C/min down to 25°C. This first applied T_S was chosen so that the polymer would only self-nucleate (i.e., T_S would be high enough to melt all the crystalline regions except for small crystal fragments and/or nuclei that can later self-seed the polymer during cooling). So, at the end of the first cooling from T_S, the polymer had been self-nucleated as in the regime II defined by Fillon *et al.* (17) for self-nucleation. Then the sample was heated in the *DSC* once again at 10°C/min but this time up to a T_S which was 5°C lower than the previous T_S. This means that the unmelted crystals at this lower T_S will anneal during the 5 min at this temperature, some of the melted species will isothermally crystallize (after being self-nucleated by the unmelted crystals) while the rest of the molten crystallizable chains (or chain segments) will only crystallize during the subsequent cooling from T_S. This procedure is repeated as indicated in Figure 1, with T_S being lowered at 5°C intervals with respect to the previous step. The chosen T_S range was 134 to 59°C for HDPE, and of 124 to 59°C for the other resins (see Fig. 1). Similarly, the melting behavior was recorded when the thermal conditioning was over, as for the previous method.

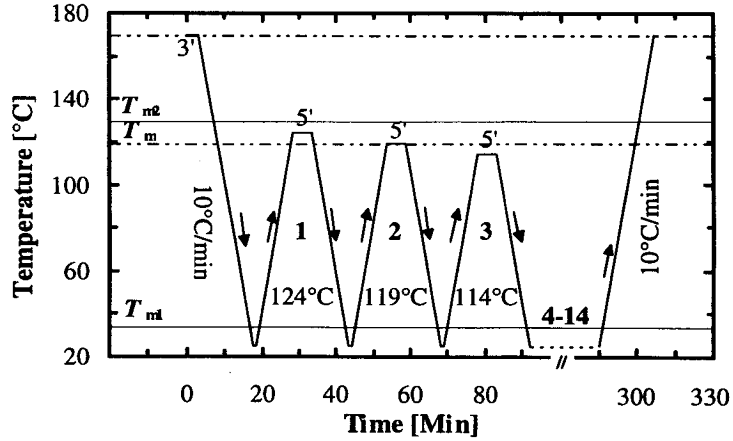

Figure 1. Schematic representation of Successive Self-Nucleation/Annealing (SSA) thermal treatment (e.g., as applied to LLDPE-b), where T_{m1} and T_{m2} define the melt range limits and T_m is the peak melt temperature (see Table 1). The T_S temperatures in the present work were varied from 124°C to 59°C at 5°C intervals for a total of 14 self-nucleating/annealing steps.

Results and Discussion

The general thermal behavior of the polymers under study is presented in Figure 2, where the crystallization during cooling from 170°C and the subsequent melting runs are shown. The differences in thermal behavior between the resins are expected in view of their branch contents and preparation methods (see Table 1). It is well known that the presence of branches within a linear PE chain is considered a structural defect since they can not normally be incorporated within the crystal lattice. Therefore, the copolymerization of ethylene with α-olefins causes a depression of both T_c and T_m with respect to the values of linear PE. Such depression of T_m depends on the comonomer content and CD, and it is generally independent of the branch length if ethyl or longer types of branches are considered (20-22). The CD is a function of the polymerization process employed to produce the copolymer and the type of catalyst used (6,8-9). This can be appreciated in Fig. 2 if the two types of LLDPE presented are examined since they were both produced by solution polymerization processes and Z-N based catalysts. The two polymers have a similar short chain branching content (see Table 1) and regardless of the comonomer type, their crystallization and melting behavior is very similar. They both exhibit broad crystallization and melting ranges with bimodal characteristics that are probably a result of a bimodal distribution of SCB (10,13-14).

The HDPE used here is also a copolymer with a high molecular weight and a bimodal distribution of molecular weights, this is reflected in the rather long tail of the crystallization exotherm (see Fig. 2*a*) that extends down to nearly 50°C from its peak value at 115°C. During crystallization at higher temperatures the shorter chains within the molecular weight distribution are being segregated and can only crystallize in that low temperature exothermic tail forming thinner lamellae that will correspondingly melt at lower temperatures (23).

The behavior of the ULDPE is very complex, it exhibits bimodal crystallization and melting signals with extremely broad transition ranges. In fact, the crystallization exotherm in Fig. 2*a* was stopped at 30°C but the crystallization could carry on if cooling continues. This gives an idea of the consequences of a high amount of chain branching, while the extremely broad crystallization range indicates the heterogeneity of CD. It is clear that the material contains a highly linear fraction capable of crystallizing at 86°C and a highly branched fraction that can only crystallize at lower temperatures. Deblieck and Mathot (11) studied by *DSC* and *electron microscopy* a VLDPE that was produced by similar polymerization methods to our ULDPE. They concluded that the material can be considered to be composed of a mixture of fractions, one fraction rich in highly branched chains with very limited if any crystallization capacity and another fraction rich in linear chains. A similar conclusion was reached by van Ruiten and Boode (24). In Fig. 2*b* it can be observed that the broad melting range extends up to 120°C indicating that a small population of thick lamellae is present in the material that could only have formed if highly linear chains were present in the ULDPE.

The VLDPE studied here is a new type of resin produced by *DOW CHEMICALS* using metallocene based catalysts (Constrained Geometry Catalyst Technology, CGCT). Such process produces a more even distribution of chain branching along the chains and a narrower distribution of molecular weights when compared to polymers obtained by Z-N based catalytic processes. In addition, CGCT catalysts differ from typical metallocene catalysts because they are able to introduce long chain branching in a controlled fashion apart from the α-olefin copolymerization. It has been established that with metallocene catalysts the linear PE resins generated usually have a narrower melting range and lower T_m values than similar density and MFI linear PE resins produced by Z-N based catalysts (8, 25-26). Even though the VLDPE used here has a higher density and crystallinity degree (see Table 1) than the ULDPE, it exhibits its main crystallization peak at lower temperatures than the ULDPE (see Fig. 2). Figure 2*b* also shows that the melting range of the VLDPE ends at approximately 105°C indicating the absence of highly linear chains that could produce thicker lamellae capable of melting at higher temperatures.

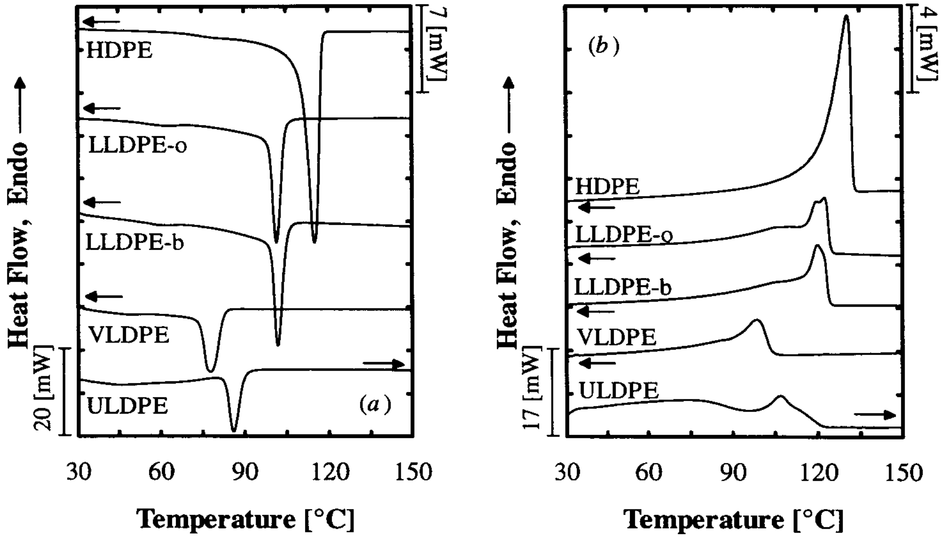

Figure 2. (*a*) Cooling DSC scans at 10°C/min after erasing thermal history at 170°C for 3 minutes and (*b*) Subsequent DSC heating runs at the same scanning rate.

Figure 3*a* compares the result of applying the SC technique to LLDPE-b with the SSA method developed here. Both methods allow the observation of structural heterogeneity in the LLDPE-b since a separation of several fractions by SCB content was made possible. However, if the two techniques are compared, it is clear from Fig. 3*a* that SSA allows better segregation and enhanced resolution. For instance, the bimodal distribution of CD (which is known to be present in this polymer by previous *TREF* results (14)) is apparent from the SSA results since a clear bimodal distribution in melting points is generated. In the case of the SC the situation is blurred by the poor separation of the high melting point fractions.

The better separation of the SSA method as compared to SC is probably due to the partial melting steps that are performed after the dynamic crystallization that follows each period at T_S. Such partial melting guarantees that only the most stable crystals remain and anneal at T_S, while the molten chains will be separated by their SCB content in view of their ability to self-nucleate and crystallize at that particular undercooling.

Figure 3b compares the SSA results obtained for the LLDPE-b with previous *TREF* results on the same polymer (14). Upon comparing the histogram of % weight *TREF* fraction distribution as a function of melting temperature with the histogram associated to the partial melting areas obtained by sequential integration of the SSA curve of Fig. 3a, it can be seen that they exhibit the same qualitative trend. The CD is bimodal in this sample. However, the *TREF* histogram is displaced to higher temperatures (e.g., the maxima in the distributions are shifted approximately 10°C with respect to one another) with respect to that based on SSA results. This shift clearly means that the separation of fractions obtained by *TREF* is probably better than that obtained by SSA since it involves crystallization from a dilute solution where molecular diffusion to the nucleating sites will not be a problem. Therefore the fractions obtained by TREF are narrower in CD and probably in molecular weight distribution also. Nevertheless, the qualitative agreement is very good considering that with SSA the fractionation is much quicker and did not involve the use of solvents at all. The quality of the fractionation with SSA can be of course improved by increasing the times at T_S and reducing the temperature intervals between T_S steps, but this will also increase the time of the measurement.

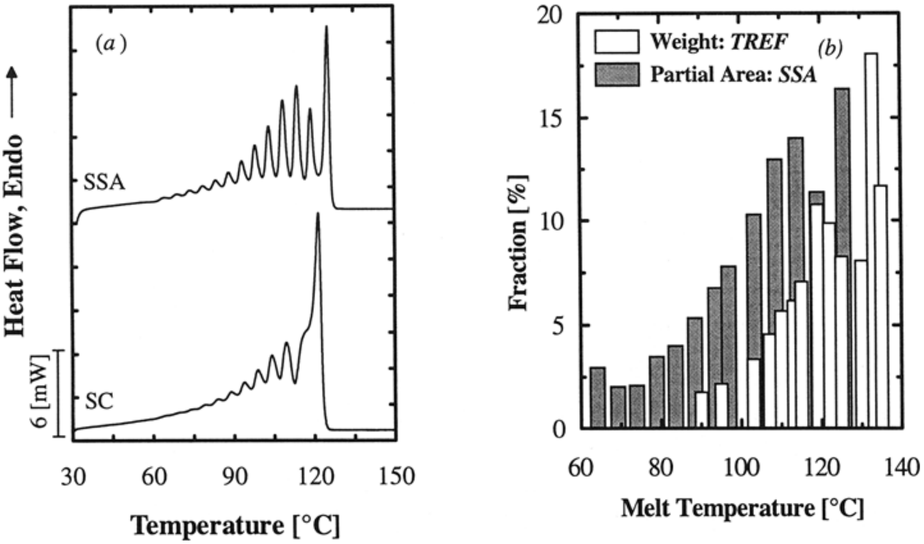

Figure 3. (*a*) *DSC* heating scans at 10°C/min after applying the following thermal treatments to LLDPE-b: *Step-Crystallization* (SC), *Successive Self-Nucleation/Annealing* (SSA). (*b*) Comparison of comonomer distributions: *TREF* vs. SSA (*TREF* data were taken from ref. 14)

The efficiency of the SSA method is also evidenced in the results of its application to ULDPE in Figure 4, where they can be compared with the results obtained by the SC technique. The difference between the two methods is even more striking in this case, since the resolution of the SSA in the separation of the linear rich fractions allows one broad peak in the SC case at high temperatures to be separated into 5 different peaks in the SSA case. Besides, the intensity and resolution of the melting endotherm of each fraction is much better in the SSA case. The fractionation could have been followed at lower temperatures but the lack of cryogenic temperature control in our equipment limited the number of steps used.

Figure 5 presents the final melting runs after applying SSA to the rest of the copolymers used in this study. The bimodal distribution of SCB is very clear in the LLDPE-o and very similar to that exhibited by the LLDPE-b (see Fig. 3) in spite of the differences in the length of the branches, as indicated above. These results are in agreement to those obtained by Starck (8) using *TREF* and SC in the same polymer, except for the better resolution shown here with SSA in comparison to his SC results.

In the VLDPE case, the fractionation by SSA clearly reveals the more homogeneous nature of the SCB distribution produced by the use of metallocenic catalysis during its synthesis. Its CD is unimodal and narrower than in any of the LLDPE or ULDPE presented above, all of which have been polymerized with Z-N based catalysts, as discussed previously.

Figure 5 also shows the results of performing SSA on the HDPE copolymer. As expected from its low branch content, this polymer possesses the narrowest distribution of lamellar thickness from all the samples examined as judged by its narrow melting range. However, several minor melting maxima were defined by the SSA treatment in the low temperature tail of the melting endotherm revealing that some fractionation was produced in the more branched and/or lower molecular weight chains of the molecular weight distribution.

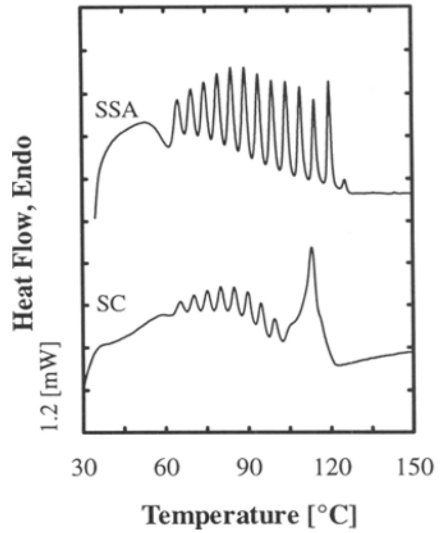

Figure 4. *DSC* heating scans at 10°C/min after applying the following thermal treatments to ULDPE: SC and SSA.

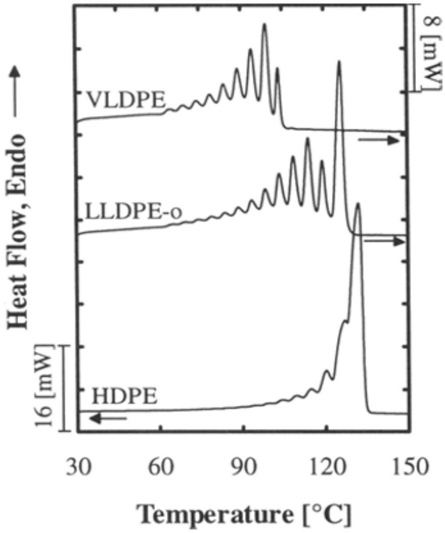

Figure 5. *DSC* heating scans at 10°C/min after applying SSA to HDPE, LLDPE-o and VLDPE

Many applications are envisaged for the SSA technique as a fast and inexpensive qualitative characterization tool. It is currently being employed to help evaluate the miscibility of linear and branched PE blends (27). It was found very helpful in revealing the structural differences between LLDPE and LLDPE functionalized with a small amount of polar groups (28) and it is being used as a valuable tool to understand the relationship between structure and morphology in crystallizable ABC triblock copolymers (29).

Conclusions

The *Successive Self-nucleation/Annealing (*SSA) technique is a useful tool to qualitatively characterize the comonomer distribution in polyethylene copolymers. The results obtained in this work indicate that SSA provides better fractionation than other similar techniques based in *Step Crystallization* (SC). The technique yields qualitatively comparable results to *TREF* but in a faster time and it does not require special instrumentation except for a conventional

DSC equipment. The SSA technique has great potential as a characterization tool of any heterogeneous system capable of crystallization, like polymer blends or block copolymers.

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References

1. Popli R, Mandelkern L (1987) J Polym Sci Polym Phys Ed 25: 441
2. Kalyon DM, Yu DW, Moy FH (1988) Polym Eng Sci 28: 1542
3. Mathot VBF, Pijpers MFJ (1990) J Appl Polym Sci 39: 979
4. Kyu B, Soo M, Mo H, Joong K, Kwon J (1992) Die Angew Makro Chem 194: 91
5. Kennedy MA, Peacock AJ, Failla MD, Lucas JC, Mandelkern L (1995) Macromolecules 28: 1407
6. Bruni C, Pracella M, Masi F, Menconi F, Ciardelli F (1994) Polym Intern 33: 279
7. Sinclair KB (1994) Plast Eng 50: 19
8. Starck P (1996) Polym Intern 40: 111
9. Kim YS, Chung CI, Lai SY, Hyun KS (1996) J Appl Polym Sci 59: 125
10. Wild L, Ryle TR, Knobeloch DC, Peat IR (1982) J Polym Sci Polym Phys Ed 20: 441
11. Mathot VBF, Pijpers MFJ (1984) Polym Bull 11: 297
12. Schouterden P, Groenickx G, Van des Heijden B, Jansen F (1987) Polymer 28: 2099
13. Hosoda S (1988) Polym J 20: 383
14. Joskowicz PL, Muñoz A, Barrera J, Müller AJ (1995) Macromol Chem Phys 196: 385
15. Kamiya T, Ishikawa N, Kambe S, Ikegami N, Nishibu H, Hattori T (1990) ANTEC Conference Procedings, pp. 871
16. Adisson E, Ribeiro M, Deffieux A, Fontanille M (1992) Polymer 33: 4337
17. Fillon B, Wittman JC, Lotz B, Thierry A (1993) J Polym Sci Polym Phys Ed 31: 1383
18. Santana OO, Müller AJ (1994) Polym Bull 32: 471
19. Morales RA, Arnal ML, Müller AJ (1995) Polym Bull 35: 379
20. Karoglanian SA, Harrison IR (1992) Thermochim Acta 212: 143
21. Woo L, Westphal S, Ling TK (1993) Thermochim Acta 226: 85
22. Alamo RG, Mandelkern L (1994) Thermochim Acta 238: 155
23. Glaser RH, Mandelkern L (1988) J Polym Sci: Part B: Polym Phys 26: 221
24. van Ruiten J, Boode JW (1992) Polymer 33: 2548
25. Butler TI, Lai SY, Patel R (1994) J Plast Film Sheet 10: 248
26. Vega JF, Muñoz-Escalona A, Santamaría A, Muñoz ME, Lafuente P (1996) Macromolecules 29: 960
27. Hernández ZH, Sánchez JJ, Arnal ML, Morales RA, Müller AJ. To be published
28. Rivero I, Márquez L, Müller AJ. To be published.
29. Balsamo V, Müller AJ, Stadler R . To be published.