Solution Crystallization Analysis by Laser Light Scattering (SCALLS)

Albert van Reenen,[*1] *Margaretha Brand,*[1] *Erich Rohwer,*[2] *Piet Walters*[2]

Summary: Solution crystallization analysis by laser light scattering offers a direct way of studying the solution crystallization of polyolefins. The technique yields similar results to Crystaf, but in a shorter time and with apparently greater sensitivity in some cases. The use of SCALLS is demonstrated for the study of selected propylene/higher α-olefin copolymers. Some conclusions are also drawn regarding the effect of molecular weight on the solution crystallization of polyolefins.

Keywords: laser light scattering; polyolefins; solution crystallization

Introduction

Crystallization from solution of the polyolefins is used in well-known analytical techniques, to provide information on chemical composition distribution of these important polymers. In this instance, both Crystaf and analytical Tref (*a*Tref) is well-known, and has been extensively reviewed.[1–4] More recently, Monrabal[5] has reported the use of Crystallization Elution Fractionation (CEF), a refinement on the basic Tref technique, and which affords rapid analysis (compared to conventional *a*Tref and Crystaf) and good separation.

Recently we reported the use of solution crystallization analysis by laser light scattering (SCALLS).[6] This technique was previously described by Shan *et al.*,[7] who initially termed the technique ''turbidity fractionation analysis''. In the case of SCALLS, light scattering can be measured (either as intensity of transmitted light or as intensity of scattered light) by taking readings (for example, based on our experimental parameters) as slowly as once every six seconds or as rapidly as ten times per second. This relates to (at a cooling rate of 1.4 °C/min and a temperature range of 70 °C) 500 to 30 000 data points. The technique also affords a direct measurement. Light is scattered as soon as crystallite sizes becomes large enough to scatter the laser light (this would be dependent on wavelength of the light). In addition SCALLS affords the opportunity of measuring the ''solution melting temperature'' of polyolefins, as the solution may be heated in a controlled fashion after crystallization has been completed. This paper reports on the effect of some of the experimental parameters as well as some recent studies on crystallization of propylene copolymers.

Experimental Part

The SCALLS Instrument

The development and layout of the instrument has been reported elsewhere.[6] We added two photodiode detectors to the instrument, at 90° and 270°. The ''in-line'' photodiode detector is denoted as the 180° detector. This detector measures laser light intensity and will record a decrease in intensity as crystallization occurs. The 90° and 270° detectors measure scattered light intensity. In a further development we placed a neutral density filter between the sample cell and the 180° detector. The general layout is shown in Figure 1.

[1] Department of Chemistry and Polymer Science, University of Stellenbosch, South Africa
E-mail: ajvr@sun.ac.za
[2] Laser Physics Institute, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

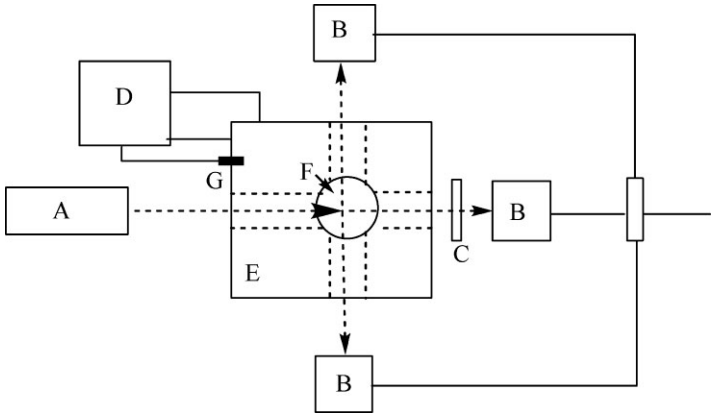

Figure 1.
A schematic layout of the SCALLS instrument. A = diode laser, B = photodiode detectors, C = neutral density filter, D = temperature controller, E = sample block, F = sample cell, G = temperature probe.

The SCALLS Method

Unless otherwise indicated, all heating and cooling experiments in the SCALLS were conducted using a polymer concentration of 1 mg/mL in 1,2,4 trichlorobenzene, and at a rate of 1.4 °C/minute. Polymer solutions were made up at 140 °C and controlled cooling was done from 100 °C to 30 °C.

Polymers

We synthesized a series of isotactic polypropylenes using a suitable C_2 symmetric metallocene catalyst. Hydrogen was used to control molecular weight. Some of these polymers were subjected to preparative TREF experiments[8] and fractions with well-defined molecular weights and tacticity were isolated and used in the molecular weight studies. The propylene copolymers (propylene/octene, propylene/tetradecene and propylene/octadecene) were synthesized using a metallocene catalyst as previously described.[9] The polymers were subjected to standard characterization techniques. Thermal analyses were done on a TA instruments Q100 DSC using a heating and cooling rate of 10 °C/min, while ^{13}C NMR spectra were obtained on a Varian VXR 600 MHz spectrometer in 1,1,2,2-tetrachloroethane-d_2, using δ 74.3 as internal secondary reference. The pulse angle was 45 degrees and the acquisition time was 0.82 seconds (130 °C) and used to determine tacticity, comonomer content and possible 2,1 monomer insertions. Molecular weight determinations were done on a PL 220 GPC at 160° in trichlorobenzene as solvent and using 4 polystyrene/divinylbenzene copolymer packed columns (PL gel MIIXED-B [9003-53-6]). The properties of the polymers that were analyzed are given in Table 1. Crystaf experiments were run on a Model 200 (Polymer Char, Valencia, Spain) in TCB as solvent (cooling at 0.1 °C/min from 100 °C to 30 °C). Where necessary, polymers were fractionated on a preparative TREF instrument built in-house.[8]

Results and Discussion

In Figure 2, the responses of the three different detectors are shown for the same polymer in the same cooling experiment. In this case, a metallocene PP with a molecular weight of 70 000 g/mol and a tacticity of 95.4% was used. There is good correlation between the three detectors. The 180° detector measures a decrease in laser light intensity, while the other two detectors measures an increase in scattered light intensity. The response for the 180° detector is reversed in the plot to allow better differentiation between the derivative curves.

Table 1.
Summary of properties of polymers used in this study.

Polymer	Mw (g/mole)	PD[b]	Comonomer type	[Comon] (mole%)
iPP-1[a]	38000 [92.7%]	2.1	None	–
i-PP-2[a]	35000 [96.6%]	2.2	None	–
i-PP-3[a]	83000 [93.5%]	1.9	None	–
i-PP-4[a]	134000 [93.5%]	2.0	None	–
PP/C8-1	506700	2.4	1-Octene	0.86
PP/C8-2	643500	2.3	1-Octene	0.57
PP/C8-3	722200	2.5	1-Octene	0.47
PP/C14-1	344800	2.5	1-Tetradecene	0.89
PP/C14-2	744900	2.5	1-Tetradecene	0.63
PP/C14-3	308900	3.0	1-Tetradecene	0.50
PP/C18-1	1140000	2.1	1-Octadecene	0.66
PP/C18-2	609000	2.5	1-Octadecene	0.47
PP/C18-3	641100	2.6	1-Octadecene	0.39

[a]: Polymer fractions obtained by p-TREF from metallocene iPP, values in square brackets are isotacticity,
[b]: PD = polydispersity

In Figure 3 and 4 we show the solution crystallization behaviour of 4 polymers obtained by the p-TREF fractionation of metallocene iPPs. In Figure 3 the solution crystallization of two polymers with similar molecular weight but different tacticities is shown. It is quite clear that the polymer with the lowest tacticity crystallizes from solution at a lower temperature, which is to be expected. In this case the molecular weight of the two polymers was quite low (around 35 000 g/mol)

In Figure 4, however, we see the crystallization behaviour of two polymers of similar tacticity (94%) but different molecular weight (83 000 vs 134 000 g/mol) In this case it seems clear that the polymer with the highest molecular weight crystallizes from solution first. The Flory Huggins equation which has commonly been adapted and used to predict the behaviour of polymers in Crystaf and TREF experiments predicts that molecular weight should not have a real effect on the solution crystallization of polyolefins. This result, as well as others that we have observed[6] seems to indicate that, in the case of PP at least, this might not be the case. ^{13}C NMR (spectra not shown

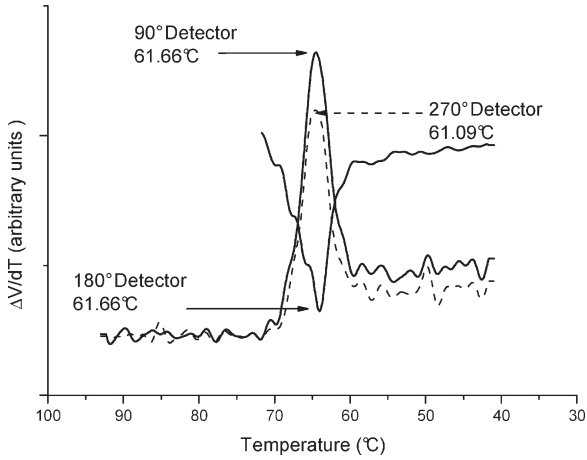

Figure 2.
First derivative SCALLS plots (cooling) of the responses of three different detectors for the same polymer sample. The 180° detector response is inverted for clarity.

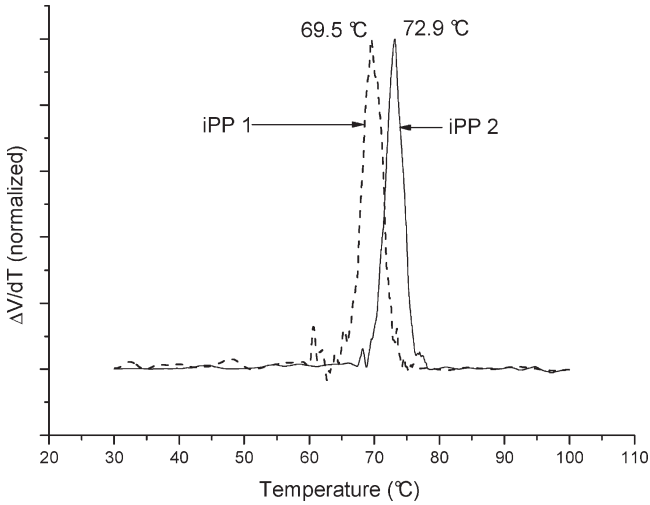

Figure 3.
The normalized first dervative SCALLS cooling plots for iPP 1 and iPP 2.

here) analysis of these two polymers reveal similar but negligible occurrence of 2,1 misinsertions in the polymers. The occurrence of these regioerrors could therefore not account for the difference in crystallization temperatures that we observe. The authors believe that crystallization is a function of both tacticity and molecular weight. Similar effects have been reported for Crystaf.[4]

We compared the use of SCALLS on a series of propylene copolymers with peak crystallization temperatures obtained by Crystaf and DSC. At the same time we also compared ''solution melting'' temperatures obtained by SCALLS with the bulk melting behaviour as measured by DSC. In Figure 5 we present the SCALLS cooling profiles of the C14 copolymers, while the Crystaf profiles for the same polymers are

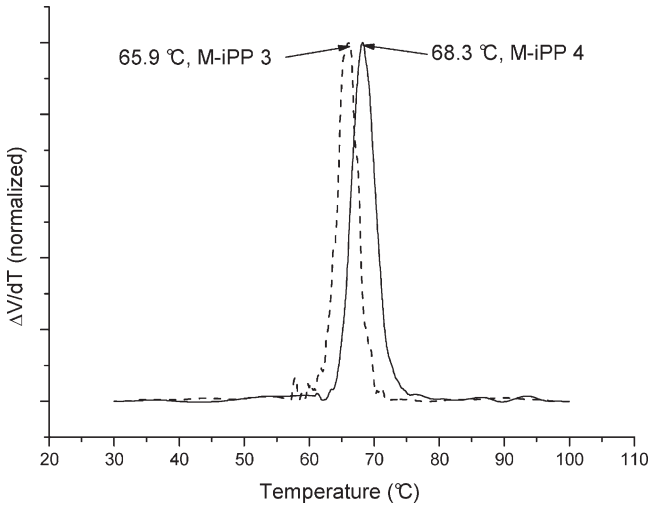

Figure 4.
The normalized first dervative SCALLS cooling plots for iPP 3 and iPP 4. Cooling rate was at 2 °C/minute for this experiment.

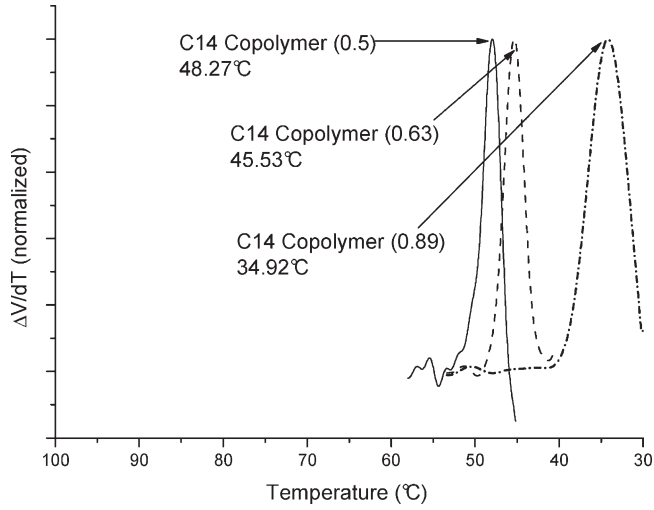

Figure 5.
The normalized first derivative SCALLS plots (ccooling) for 3 C14 copolymers. Comonomer content and peak crystallization temperatures are indicated on the figure.

presented in Figure 6. In this instance, it is interesting to note that SCALLS is able to differentiate between two polymers with small differences in comonomer content (see Table 1) while this appears to be difficult to do with Crystaf. A graphic summary of all the results of this study is presented in Figure 7. Overall the peak crystallization temperatures determined by SCALLS is lower than for Crystaf, largely due to the faster cooling rate used for SCALLS.

In Figure 8 the cooling profile of the C18 copolymers are presented, with the heating profile of the three polymers presented in Figure 9. It is clear that SCALLS

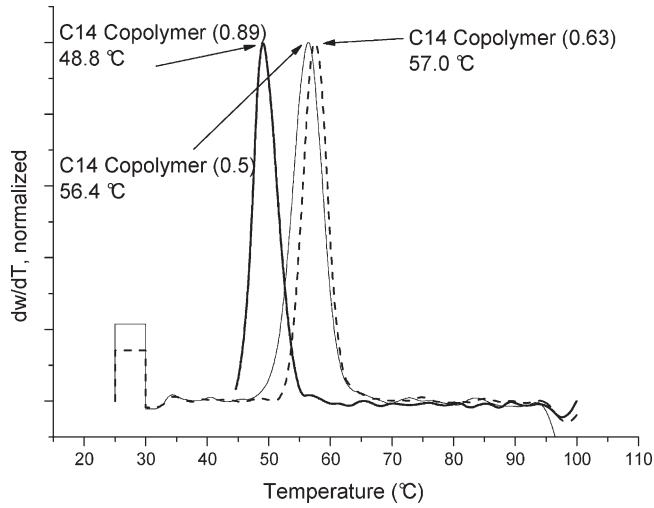

Figure 6.
The Crystaf cooling profiles for 3 C14 copolymers. The peak crystalization temperatures and the comonomer content are indicated in the figure.

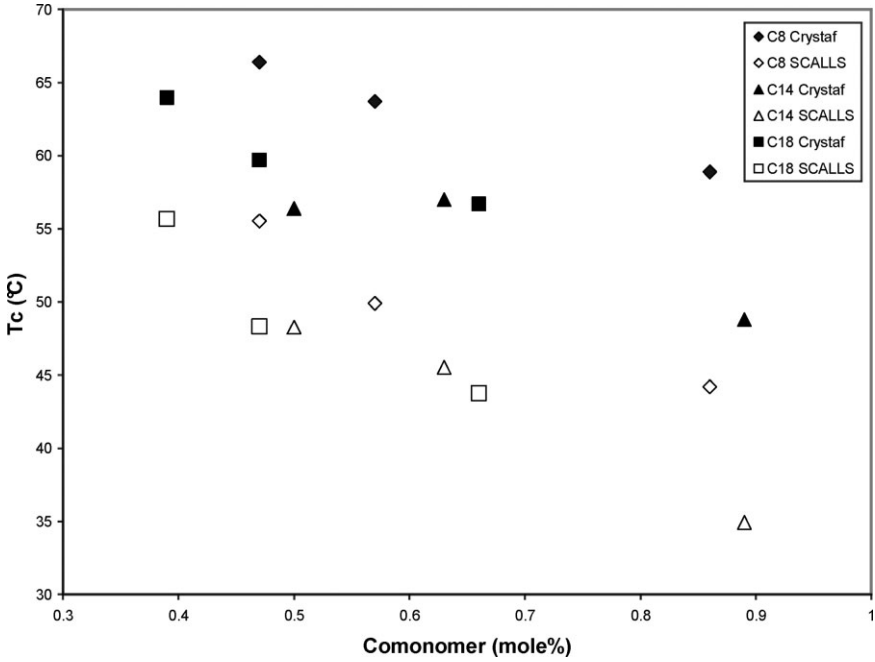

Figure 7.
The peak solution crystallization temperatures of propylene copolymers (C8, C14 and C18) as determined by SCALLS and Crystaf.

presents an opportunity to study the ''solution melting'' behaviour of the polyolefins. A comparison of the solution and DSC melting trends for the C18 and C14 copolymers are presented in Figure 10. A good correlation is observed. It should be possible to study the relationship between the solution melting (T_m) and the bulk melting temperature (T_m^0) as a function of comonomer type and content.

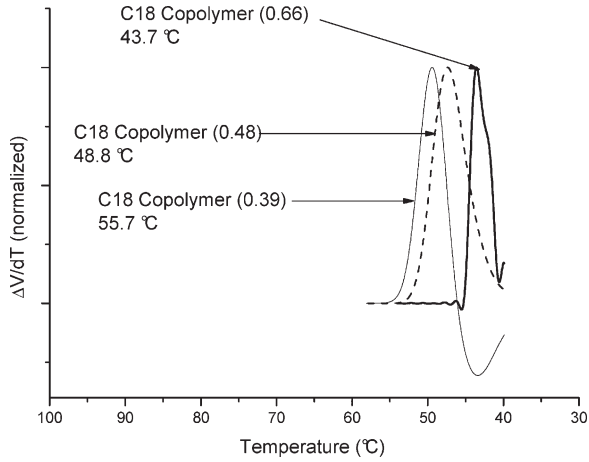

Figure 8.
Normalized first derivative SCALLS plots (cooling) for propylene-octadecene copolymers. The peak crystallization temperatures and the comonomer content are shown in the figure.

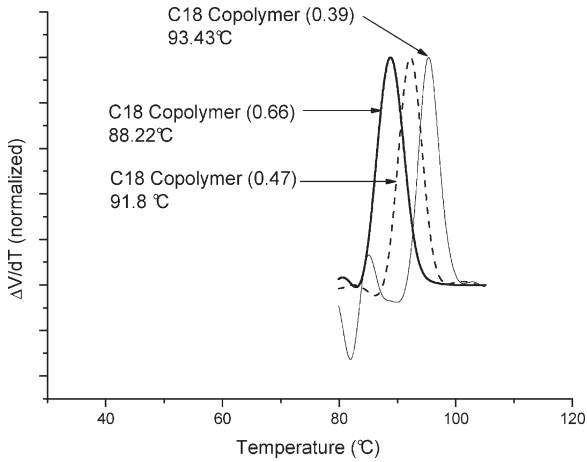

Figure 9.
The normalized first derivative SCALLS plots (heating) for propylene-octadecene copolymers. The peak crystallization temperatures and the comonomer content are shown in the figure.

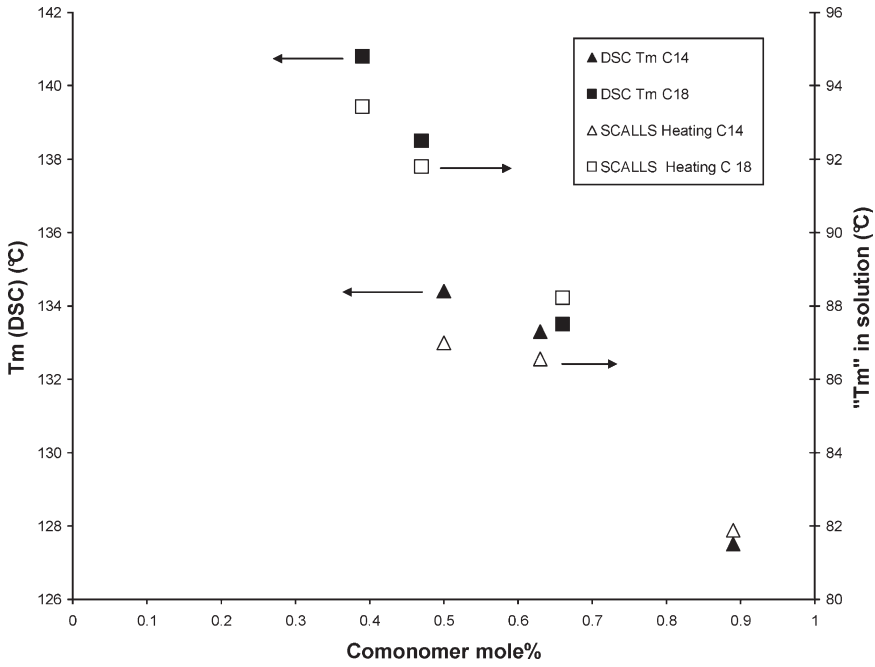

Figure 10.
Comparison of DSC melting temperatures and SCALLS solution melting temperatures for C18 and C14 propylene copolymers.

The data presented here is obviously insufficient to draw conclusions from, but we are at present completing a series of similar measurements on a wide range of propylene-1-alkene copolymers, and will be presenting the results shortly.

Conclusion

SCALLS is a direct method of observing solution crystallization of the polyolefins. The technique is able to clearly differentiate in the crystallization behaviour of

polyolefins with small but distinct differences in chemical composition. In some instances this technique, even with rapid cooling rates, appears to be more sensitive than Crystaf. This could be due to the fact that this is a direct method, which records changes in light intensity and scattering immediately, while Crystaf relies on far fewer measurements which occur after the fact. In Crystaf crystallization occurs first, and thereafter a solution concentration is measured. The authors also believe that SCALLS presents a means of directly investigating the applicability of the Flory-Huggins equation to the prediction of solution crystallization of the polyolefins, in particular the effect of molecular weight and even the solution interaction parameter.

[1] S. Anantawaraskul, J. B. P. Soares, P. M. Wood-Adams, *Adv. Polym. Sci.* **2005**, *182*, 1.
[2] J. B. P. soares, A. E. Hamielec, in: "*Modern techniques for polymer characterization*", R. A., Pethrick, J. V. Dawkins, Eds., Wiley, New York 1999, p. 15.
[3] L. Wild, C. Blatz, in: "*New advances in polyolefins*", T. C. Chung, Ed., Plenum, New York 1993, p. 147.
[4] J. B. P. Soares, S. Anantawaraskul, *J Polym. Sci. B: Polym. Phys.* **2005**, *43*, 1557.
[5] B. Monrabal, J. Sancho-Tello, N. Mayo, L. Romero, *Macromol. Symp.* **2007**, *257*, 71.
[6] A. J. van Reenen, E. Rohwer, M. Brand, M. Lutz, P. Walters, *J. Appl. Polym. Sci.* **2008**, *109*, 3238.
[7] C. L. P. Shan, W. A. deGroot, L. G. Hazlitt, D. Gillespie, *Polymer* **2005**, *46*(25), 11755.
[8] A. J. van Reenen, G. W. Harding, *Macromol. Chem. Phys.* **2006**, *207*, 1680.
[9] A. J. van Reenen, R. Brüll, U. M. Wahner, H. G. Raubenheimer, H. Pasch, *J. Polym. Sci A: Polym. Chem.* **2000**, *38*(22), 4110.

