

FRACTIONATION OF HDPE ON QUENCH COOLING

Claudia A. Fonseca and I. R. Harrison

The Pennsylvania State University, Department of Materials Science and Engineering,
325 Steidle Building, University Park, PA 16802, USA

Abstract

In a previous paper we discussed co-crystallization in a LDPE/HDPE blend using TREF and DSC. As part of that study it was observed that pure HDPE showed an unexpected fractionation behavior when quench crystallized in TREF. The overall peak broadened and two peaks appeared instead of the previously observed single peak for slow cooled HDPE.

The development of two peaks was observed for all commercial HDPEs investigated, independent of their melting indices and densities. TREF and GPC were used in an attempt to evaluate the origin of the two HDPE components.

Keywords: HDPE, quench cooling, TREF

Introduction

Numerous studies reported in the literature show that there is a tendency for polymer chains to demonstrate less segregation when rapidly crystallized from the melt [1-4]. Investigators studied crystallization from the melt of binary mixtures of linear polyethylene fractions [1] and reported that there was no fractionation within these mixtures following quench crystallization. In other work [5], isothermal crystallization data for melts showed that as crystallization temperature is lowered, linear polyethylene chains with different molecular weights tend to crystallize simultaneously.

In the present study, LDPE and HDPE were investigated using Temperature Rising Elution Fractionation (TREF), which separates semi-crystalline polymer chains based on relative crystallizability of molecules. In standard/regular TREF, polymer is dissolved in a solvent at high temperature. An inert support is added, and the mixture is then slowly cooled, allowing polymer molecules to crystallize on the support according to their crystallizabilities. After crystallization the temperature is raised continuously with solvent flowing. Chains which crystallized with difficulty (branched or otherwise defective chains) are eluted first (at lower temperatures). As the temperature rises less defective, more perfect chains are eluted. In this work, an alternative mode of crystallization was used, the polymer was quench crystallized from solution. As a result HDPE showed unexpected fractionation behavior with the development of two elution TREF peaks instead of the single peak observed when slow cooling crystallization was applied. TREF and GPC were used in an attempt to determine the causes of this phenomenon.

Experimental

Polymers used in this work were supplied by Dow Chemical Company and identified as LDPE 526; HDPEs 12165, 4352N, 8354N and 10062N. Narrow molecular weight HDPE fractions were also provided by Dow Chemical. Some of the reported physical properties of commercially available materials are listed in Table 1.

Table 1 Homopolymer data

Polymer	Dow product	Density* / g cm ⁻³	Melt index* g 10 min ⁻¹
LDPE	526	0.919	1
HDPE	4352N	0.952	4
HDPE	8354N	0.954	7
HDPE	10062N	0.962	10
HDPE	12165	0.965	0.9

*As reported in Dow Chemical product literature.

Polymers supplied as pellets were first molded into thin films using a Carver press at 160°C and a pressure of 10000 psi. Polymers supplied as powder were used as received. Solutions of approximately 1% w/v polymer/solvent were prepared at 140°C using 1,2,4-trichlorobenzene (TCB) as solvent; 2,6-di-tert-butyl-4 methylphenol (BHT) was added at a concentration of 0.1% to prevent degradation of the polymer. After dissolution, previously heated (140°C) inert support (glass beads) was added to the polymer solution, producing a sludge like mixture.

Subsequently, one of two different modes of crystallization were applied. In the standard or slow cooled (SC) TREF procedure, the sample vial was loaded into a preheated crystallization oven (130°C) and a very slow cooling rate (1.5°C h⁻¹) was applied to the sample. Alternatively, the polymer was quench crystallized (Q), that is the hot sample vial was immediately placed in either an ice-water or liquid nitrogen bath. Subsequently, the mixture was loaded into a column, and placed in an elution oven. A temperature ramp was applied to the oven while simultaneously TCB was pumped through the column. Eluting solution flows to an IR detector to determine the concentration of polymer in the solution.

Two modes of TREF were used. The analytical mode has a sample size in the range of 30–60 mg, solvent flow rate: 4 ml min⁻¹ and a heating rate of 40°C h⁻¹. Preparative TREF uses a sample size of 1.0 g, solvent flow rate: 8 ml min⁻¹ and a heating rate of 20°C h⁻¹. This larger sample size made possible the separation of fractions of the original polymers in amounts necessary for further characterization. Preparative TREF fractions were typically further analyzed by analytical TREF and GPC.

Results

When low density polyethylene is quenched in a TREF experiment, the elution curve is narrower than in the slow cooled case. Presumably, fractionation on

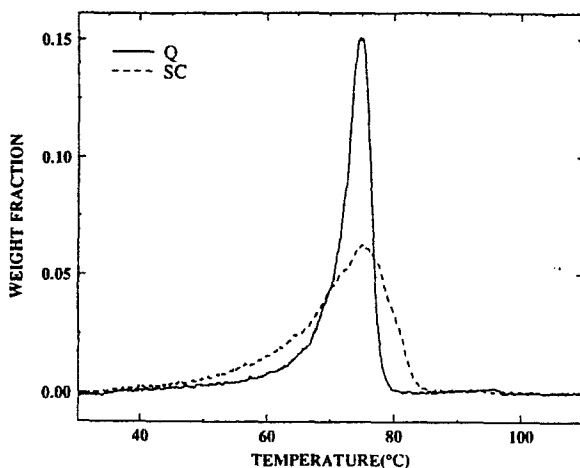


Fig. 1 Analytical TREF of LDPE

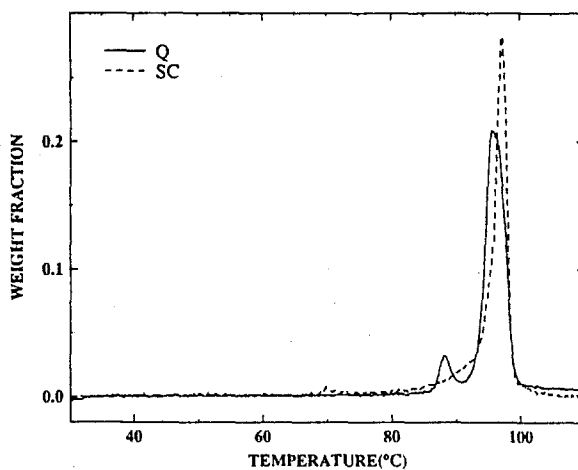


Fig. 2 Analytical TREF of HDPE

quenching is not as efficient as the slow cooled case (Fig. 1). In contrast, pure HDPE 12165 showed unexpected behavior when quenched for TREF (Fig. 2). The overall peak broadened and more importantly two peaks appeared instead of the single peak observed for slow cooled HDPE. As observed in Fig. 3, the development of two peaks appears to be general for all HDPEs investigated, independent of their melt indices and densities, although the higher temperature peak shifts to higher temperatures with increasing density. Furthermore, HDPEs 10062N and 12165 have comparable densities but widely different melt flow indices, 10 and 0.9 respectively, yet both show two peaks of comparable relative areas.

In an effort to determine the causes of this phenomenon, preparative TREF was performed on HDPE 12165 using quench crystallization. The materials associated

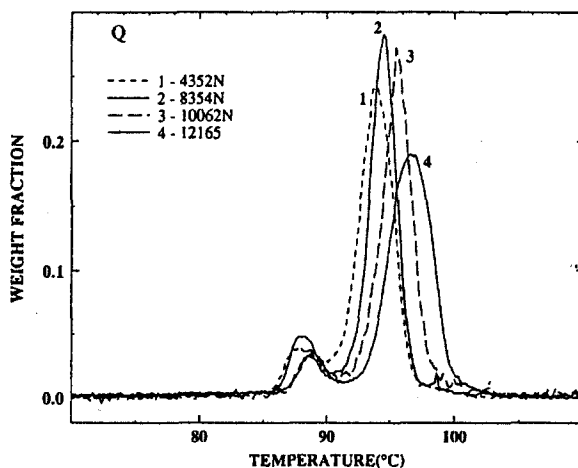


Fig. 3 Analytical TREF of various quenched commercial HDPEs

with the two peaks were isolated and, subsequently, analyzed using standard slow cooled analytical TREF and GPC. Figure 4 shows the slow cooled analytical TREF curve of the low and high temperature quench TREF fractions. The TREF curve of the original sample is included for comparison. Curves have been scaled according to the ratio of components present in the original polymer. It appears that the isolated materials are associated with two different portions of the original whole HDPE material. This result supports the possibility that some type of segregation among HDPE molecules is occurring on quenching.

Table 2 shows GPC data for the two quenched TREF fractions as well as for the original HDPE 12165. The low temperature fraction has a significantly lower molecular weight while the high temperature fraction has higher molecular weight.

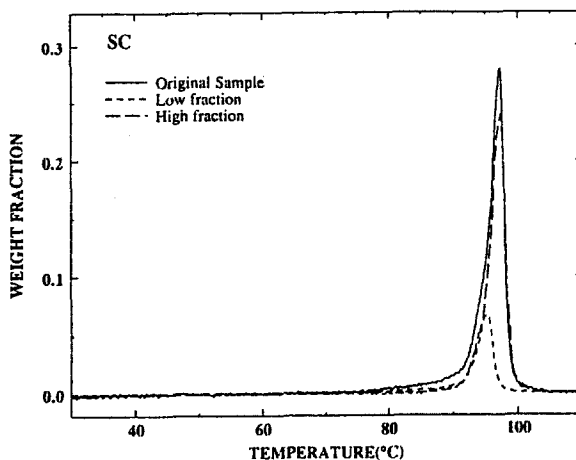


Fig. 4 Analytical TREF of standard crystallized HDPE fractions

Table 2 GPC data for original HDPE 12165 and its fractions

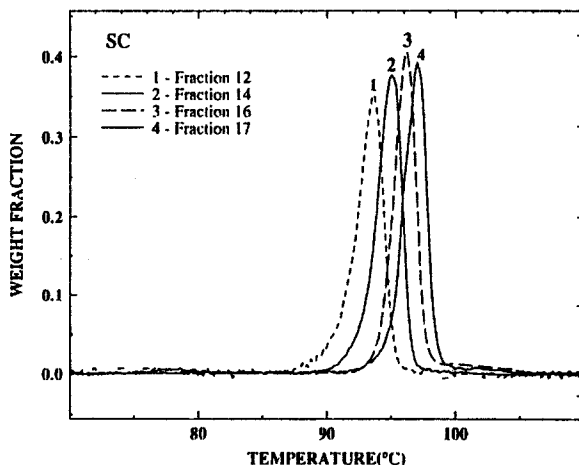
HDPE 12165	Mn	Mw	Mz	Mw/Mn
Original	25100	83600	239600	3.33
Lower fraction	14600	56100	249300	3.96
Higher fraction	41800	94600	232900	2.44

Table 3 GPC data for narrow molecular weight HDPE fractions

Fractions	Mn	Mw	Mv	Mw/Mn
12	12300	14100	13800	1.15
14	22300	25500	25100	1.14
16	46000	53400	52400	1.16
17	70400	116000	104000	1.65

This GPC data immediately raises the possibility that molecular weight segregation is taking place when HDPE is quenched in TREF.

A series of linear narrow molecular weight fractions of HDPE were investigated using TREF. Molecular weight data for these fractions are reported in Table 3. TREF data for the fractions after slow crystallization is illustrated in Fig. 5. Elution temperature increases as molecular weight increases and is consistent with an earlier report by Wild *et al.* [6].

**Fig. 5** Analytical TREF of standard crystallized narrow molecular weight HDPE fractions

TREF elution curves for the fractions after being quenched in liquid nitrogen are shown in Fig. 6. Compared to slow crystallized samples, the quenched fractions show broader peaks. In addition, the dissolution temperatures (peak maximum) for

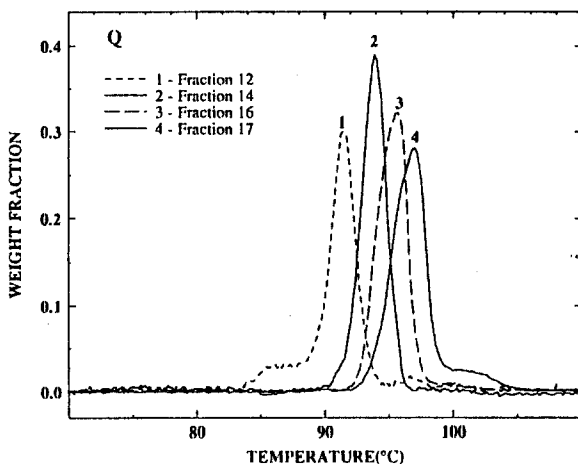


Fig. 6 Analytical TREF of quenched narrow molecular weight HDPE fractions

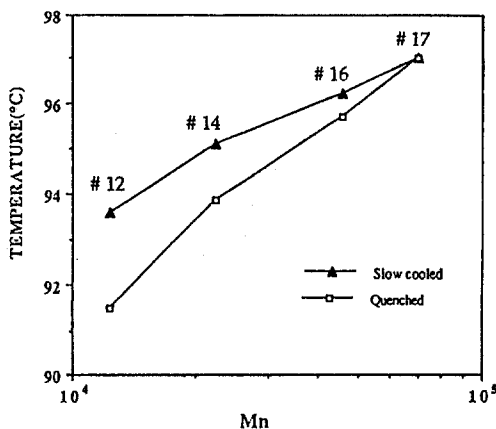


Fig. 7 Effect of molecular weight on TREF elution temperatures of narrow molecular weight HDPE fractions

quenched samples of the four narrow fractions are more widely separated than for slowly crystallized fractions. This observation is more evident when elution temperature vs. M_n is plotted as shown in Fig. 7.

The difference in elution temperature for slow cooled fractions 12 and 17 is 3.5°C , while for quenched fractions, the difference increases to 5.6°C . This observation suggests that better molecular weight segregation is obtained when HDPE is quenched from solution. For molecular weights higher than $\approx 7.0 \times 10^4$ no segregation between slow cooled and quenched samples is obtained.

Discussion

One possible explanation for this fractionation phenomenon in HDPE is that TREF data for quenched HDPE is showing a melting-recrystallization-melting phenomenon. Imagine that when a semi-crystalline polymer is supercooled, very imperfect crystals are formed. Upon heating, these crystals melt at a temperature significantly below T_m^0 , the equilibrium melting temperature. The melt can recrystallize to more perfect crystals, which in turn can melt at higher temperatures. This phenomenon gives rise to multiple melting peaks and was detected for crystals grown from polymer solutions and melts [7, 8]. While such a picture is applicable to DSC, from the point of view of the TREF technique, melting-recrystallization-melting must be rejected. TREF consists of dissolution of previous crystallized polymer with solvent flowing continuously. Therefore, when an elution peak is registered, it means that the material associated with it has already eluted off the column and reached the detector. It is therefore not possible that such material recrystallizes and melts again at higher temperature. Furthermore, the TREF elution heating rate was decreased by half and no change in the two peaks areas was observed.

Another possible explanation is that reorganization involving no melting of the original crystallites takes place undetected on the TREF column; i.e., thickening during the elution step. In this model, initially imperfect crystallites formed during the quenching process thicken at different rates, resulting in the development of multiple peaks. However, when the TREF elution heating rate was decreased by half, no change in the area associated with the two peaks was observed. If thickening of the crystals was taking place, heating at slower rates should increase the amount of thickening and we would anticipate a decrease in the first peak area with a subsequent increase in the second.

The presence of two melting peaks associated with segregation of molecular weight was observed by some investigators [9]. They studied isothermal crystallization from the melt and melting behavior of mixtures of narrow molecular weight poly(ethylene oxide) fractions by DSC. For some crystallization temperatures, two melting peaks were observed, each peak being associated with lower and higher molecular weight fractions. However, no segregation was observed at low crystallization temperatures where crystallization rates are higher. This latter behavior is in complete contrast with that observed in a TREF experiment, where rapid cooling and presumably lower crystallization temperatures promote segregation.

Clearly there are problems with those explanations suggested so far. The correct explanation for this phenomenon may lie in the nature of the crystallization process from solution. Dilution, thermal conditions and solvent power play fundamental roles in the crystallization process from solution. Phase equilibrium diagrams for crystallizable polymers in poor solvents exhibit both liquid-liquid demixing and polymer crystallization. DSC studies using ramp cooling in the region of the phase diagram where liquid phase separation precedes crystallization, revealed two exothermic peaks reflecting crystallization from two discrete liquid phases [10]. For solutions of linear PE in a good solvent, liquid phase separation should be strictly

excluded, since there is no regime of liquid phase separation reported anywhere in the equilibrium phase diagram. However, Lee *et al.* [11] studied i-PP in solvents with different powers and found that for a system with strong interactions, although there was no region of liquid-liquid coexistence in the equilibrium phase diagram, a region of liquid instability with phase separation may be accessed by suitably fast cooling. Since the experiments in this present work were performed in nonequilibrium conditions, similar 'hidden' binodals may explain the discrete crystallization of the two different components of HDPE. It is possible that polymer chains are unevenly distributed with respect to molecular weight between two liquid phases. Such a distribution could lead to the observed TREF behavior.

* * *

The authors appreciate support from CAPES-BRAZIL (C.A.F.). Additional thanks go to Dr. G. W. Knight in Dow Chemical Company for kindly providing the polymer samples and performing the GPC analysis.

References

- 1 R. H. Glaser and L. Mandelkern, *J. Polym. Sci.: Part B: Polym. Physics*, 26 (1988) 221.
- 2 T. Sato and M. Takahashi, *J. Appl. Polym. Sci.*, 13 (1969) 2665.
- 3 M. P. Farr and I. R. Harrison, *Polymer Preprint*, 31 (1990) 257.
- 4 M. P. Farr, Ph.D Dissertation, The Pennsylvania State University, 1991.
- 5 E. Ergoz, J. G. Fatou and L. Mandelkern, *Macromolecules*, 5 (1972) 147.
- 6 L. Wild, T. R. Ryle, D. C. Knobloch and I. R. Peat, *J. Polym. Sci.: Polym. Phys. Ed.*, 20 (1982) 441.
- 7 H. Phuong-Nguyen and G. Delmas, *Thermochim. Acta*, 238 (1994) 257.
- 8 R. Alamo and L. Mandelkern, *J. Polym. Sci.: Part B: Polym. Phys.*, 24 (1986) 2087.
- 9 S. Z. D. Cheng and B. Wunderlich, *J. Polym. Sci.: Part B: Polym. Phys.*, 24 (1986) 577.
- 10 J. L. Zryd and W. R. Burghardt, *J. Appl. Polym. Sci.*, 57 (1995) 1525.
- 11 H. K. Lee, A. S. Myerson and K. Levon, *Macromolecules*, 25 (1992) 4002.