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WORKING PARTY ON MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS*

MOLECULAR CHARACTERIZATION OF ETHYLENE-PROPYLENE BLOCK COPOLYMERS

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MOLECULAR CHARACTERIZATION OF ETHYLENE-PROPYLENE BLOCK COPOLYMERS

Abstract - In order to improve Polypropylene impact strength at low temperature, the process of copolymerizing propylene with ethylene is industrially used. Through a proper program of interlaboratory tests, the best method both for the isolation of the copolymeric fraction and the homogeneity of the molecular characterization data were investigated.

1. INTRODUCTION

It is known that homopolymeric polypropylene shows an unsatisfactory impact strength at low temperature, due to its relatively high glass transition temperature. In order to improve this property, the process of copolymerizing propylene with proper amounts of ethylene is used industrially. Two types of polypropylene crystalline copolymers are produced industrially depending on the type of technology employed, i.e.:

- the "random" copolymers, in which ethylene is incorporated along the polymeric chain, in a statistical manner,
- the so-called "block" copolymers, in which a copolymeric elastomeric fraction results, incorporated with the residual homopolymeric fraction.

A great deal of literature (refs. 1-6) is available correlating composition and morphology of the block copolymers with their properties.
This work, through a proper programme of interlaboratory tests, aims to investigate the best methods both for the isolation of the elastomeric fraction, on the one hand, and the confirmation of the significance of the molecular characterization data obtainable on these fractions, on the other.
For this purpose, two samples of block copolymers, commercially available from DSM and SAGA, were analysed and two different fractionation systems (hot heptane extraction, cold xylene solubility) were performed.
The fractions were characterized using different methods (I.R., NMR, DSC, Viscosimetry, Light Scattering, GPC).

2. EXPERIMENTAL

(2.1.) Fractionation of block copolymers

Pellets were pressed into 100 ± 20μm thick films in a hydraulic press at around 200°C for about 1 min.

(2.1.1.) Heptane extraction - Films were extracted for 6 h at 98.4°C under a nitrogen atmosphere reflux and then rinsed and dried under vacuum at 50°C. The solution was cooled at 25°C and filtered. The precipitate was washed with n-heptane and acetone and dried in a vacuum oven at 50°C. The filtrate was slowly poured out into acetone. After filtration the polymer was washed with acetone and dried under vacuum at 50°C.

(2.1.2.) Films were dissolved in xylene (5 g/l)at 135°C for 2 h. The solution was slowly cooled at room temperature, stored for 24 h, and filtered. The precipitate was washed with n-heptane and acetone, and dried under vacuum at 50°C. The filtrate was slowly evaporated and dried under vacuum at 50°C.

(2.2.) Intrinsic viscosity η

Samples were dissolved at 160°C for 2 h in trichlorobenzene (TCB) (sample concentration = 0.5 mg/ml), in the presence of traces of antioxidants.
Measurements were carried out at 135°C in TCB.

(2.3.) Light Scattering

Measurements were carried out according to the following conditions :

Laboratory	Solvent	Temperature	dn/dc	Dissolution
HÜLS	n-decane	135°C	0.100	2 h - 160°C
DSM	αClN	160°C	0.184	2 h - 160°C
BASF	αClN	150°C	0.184	2 h - 150°C
ME-FERRARA	αClN	150°C	0.189	2 h - 150°C
SOLVAY	αClN	145°C	0.189	2 h - 150°C
ME-NOVARA	αClN	150°C	0.189	2 h - 150°C

(2.4.) GPC analysis

Measurements were carried out according to the following conditions :

Laboratory	Instrument	Solvent	Temperature
HÜLS	not specified	αClN	140°C
BASF	" "	TCB	150°C
DSM	Waters 200	TCB	140°C
ME-FERRARA	" "	ODCB	135°C
SOLVAY	not specified	TCB	135°C
ME-NOVARA	Waters 200	ODCB	135°C
NESTE-OY	" "	TCB	138°C
CHALMERS T.H.	" "	TCB	135°C
BP CHIMIE	Du Pont 860	TCB	150°C
C.d.F. CHIMIE	not specified	TCB	135°C

(2.5.) Ethylene content of block copolymers

Both NMR and IR techniques were used for determining the ethylene content of the block copolymers.
Some laboratories also investigated the contents of block and randomly distributed ethylene units (see appendix 1).

(2.6.) Thermal analysis

Measurements were carried out at heating and cooling rates of from 5°C/min (DSM) to 20°C/min (Solvay).

C.d.F. Chimie = 8°C/min; Chalmers = 10°C/min; ME/Ferrara and BP Chimie = = 16°C/min.

Tm^B = temperature of melting peak from second heating curve
Tc = crystallization peak temperature from cooling curve
Tg = glass transition temperature.

3. ETHYLENE-PROPYLENE BLOCK COPOLYMERS RESULTS

Characterization results (η , IR, NMR, GPC, LS, DSC) of the whole samples of the DSM and SAGA copolymers are reported in Table 1.
Characterization results on xylene soluble and insoluble fractions of the DSM and SAGA copolymers are reported in Table 2 and Table 3 respectively.
Characterization results on heptane soluble and insoluble fractions of DSM and SAGA copolymers are reported in Table 4 and Table 5 respectively.
NMR results are reported in Appendix 1.

TABLE 1

SAMPLE EP COPOLYMER (DSM)

LABORATORY	η_{TCB} 135°C dl/gr	IR wt% C_2	NMR wt% C_2	GPC $\bar{M}w$ 10^{-3}	GPC $\bar{M}n$ 10^{-3}	L.S. $\bar{M}w$ 10^{-3}	DSC: Tm_1B Tm_2B °C	DSC: Tc °C	DSC: Tg °C	DSC: δH J/g
ME - FE	2.05	9.8		362	38.3	295	122-162	112		
HÜLS	1.89	9.4	10.4	405	42.5	540	125-164			92
NESTE-OY	1.97	9.1	9.5	410	30		121-161			80
CHALMERS T.H.	2.04	7.6 *		404	24		125-167			
SOLVAY	2.12	6.0	8.6	439	43	417	122-162	108		87
BP-CHIMIE										
D S M	2.10		8.7	450	27	400	124-164	106-125		100
B A S F	2.09	9.0	10.5	486	66	447		114		
C D F				419 (PE)	26.4 (PE)		124-164			81
ME - NO	2.07			322	32	254				
UNILEVER	1.41	8.5								
SAMPLE EP COPOLYMER (SAGA)										
ME - FE	2.05	6.3		366	68.3	370	122-163	113-90		
HÜLS	1.86	6.0	7.8	392	55	500	124-163			90
NESTE-OY	2.00	5.8	5.7	380	49		121-162			78
CHALMERS T.H.	2.08	4.4 *		404	44		124-166			
BP-CHIMIE	2.15	10.5		300	58		120-146-160	113-99		
SOLVAY	2.15	4.0	6.8	452	70	444	122-163	113		82
D S M	2.03		6.9	420	44	450	165	123		96
B A S F	2.1	6.4	7.1	440	62	480	122-165	116		
C D F										
ME - NO	2.14			359	72	345				
UNILEVER	1.99	6.7								

* $\%(CH_2)n \geqslant 5$

TABLE 2

SAMPLE EP COPOLYMER (DSM) XYLENE SOLUBLE 25°C

LABORATORY	wt%	η TCB 135°C dl/gr	IR wt% C_2	NMR wt% C_2	GPC $\overline{Mw}$ 10^{-3}	GPC $\overline{Mn}$ 10^{-3}	L.S. $\overline{Mw}$ 10^{-3}	DSC Tm_1B Tm_2B °C	DSC Tc °C	DSC Tg °C	DSC δH J/g
ME - FE	8.2+0.5 (oils)	5.80	51.5		544 (EP)	82 (EP)		76			
HÜLS	8.0		50	40	290 (EP)	14.7 (EP)		53		-57 -50	
NESTE-OY	7.2				424	6					
CHALMERS T.H.	8.0		38.7*					43-157			
SOLVAY	7.6		49	41.7	442(PE) 683(PP)	5.7(PE) 21(PP)		30-50	90-25	-49 -31	1.5
D S M	7.7	5.58		46.5	1110	35				-56 -8	
B A S F	8.5	4.8			>1000						
C D F	8.2										
XYLENE INSOLUBLE 25°C											
ME - FE	91.3	1.89	5.8		306	30.2		122-162	111		
HÜLS	92		5.7	5.5	221	37.5		161			94
NESTE-OY	92.8		6.7		341	27.5		122-163			79.6
CHALMERS T.H.	92	1.84	5.3*		338	24		123-163			
SOLVAY	92.4		5.0	4.5	347	42		124-166	112		97
D S M	92.3	1.74		7.6	397	27		124-163	111-121		103
B A S F	91.5	1.90	6.5								
C D F	91.8							124-163	110-115		

* $\%(CH_2)n \geqslant 5$

TABLE 3

SAMPLE EP COPOLYMER (SAGA) XYLENE SOLUBLE 25°C

LABORATORY	wt%	η_{TCB} 135°C dl/gr	IR wt% C_2	NMR wt% C_2	GPC $\bar{M}w$ 10^{-3}	GPC $\bar{M}n$ 10^{-3}	L.S. $\bar{M}w$ 10^{-3}	DSC Tm_1B Tm_2B °C	DSC Tc °C	DSC Tg °C	DSC δH J/g
ME - FE	11.6+0.9 (oils)	3.42	36		398 (EP)	68 (EP)		76			
HÜLS	12		37	31.4	131 (EP)	5.4 (EP)		46		-50 -58	
NESTE-OY	11.9				407	8					
CHALMERS T.H	8.3		33.8*					42-152			
SOLVAY	11.9		40	30.4	362(PE) 559(PP)	13(PE) 38(PP)		57	71-19	-47 -22	2
D S M	11.6	3.24		32.8	645(PP)	33(PP)				-55 -12	
B A S F	11.0	2.95	30								
XYLENE INSOLUBLE 25°C											
ME - FE	87.5	1.97	3.0		369	63.6		122-162	112		
HÜLS	88		6.9	4.8 block	271(EP)	6.9 (EP)		126-162			93
NESTE-OY	88.1		4.9		346	44		163			88.7
CHALMERS T.H.	91.7	2.00	5.1*		402	51		122-158 163			
SOLVAY	88.1		3.0	2.9	431	74		125-165	111	-11 -5	90
D S M	88.4	1.86		4.0	375	38		124-163	113-122		91
B A S F	89	2.2	3.6								

* $\%(CH_2)n \geq 5$

TABLE 4

SAMPLE EP COPOLYMER (DSM) HEPTANE SOL.98°C(a);INSOL.25°C(b); SOL. 25°C(c)

LABORATORY	wt%	η_{TCB} 135°C dl/gr	IR wt% C_2	NMR wt% C_2	GPC $\bar{M}w$ 10^{-3}	GPC $\bar{M}n$ 10^{-3}	L.S. $\bar{M}w$ 10^{-3}	DSC Tm_1B Tm_2B °C	DSC Tc °C	DSC Tg °C	DSC δH J/g
ME - FE	5.1(b) 4.4(c)	1.98(b) 2.48(c)	41(b) 40(c)					109-134(b) 110(c)	97(b) 50(c)		
HÜLS	3.8(c) 3.7(c)		33(c)	36.7(c)	393(EP) (c)	35.5 (c)		48-58(c) 119 (c)		-48(c) -56(c)	
NESTE-OY	9.5(a)		43(a) 10(b)		211(a)	7(a)		114-137(b) 156(b)			
CHALMERS T.H.	2.0(b) 11.2(c)		35.2* (c)					41-145(c)			
SOLVAY	6.1(b) 5.2(c)		14.0(b) 41.0(c)	16.9(b) 31.5(c)				122-155-160 113 (c)	108(b) 102(b)	-46(c) -30(c)	90(b) 12(c)
D S M	4.05(b) 3.9(c)	1.02(b) 2.46(c)		22(b) 34.2(c)	255(b) 406(c)	9.0 (b) 10(c)		119-153-161 125 (c)	104(b) 120(b) 97 (c)	no Tg -56(c) -5 (c)	80(b)
UNILEVER	11.4(a) 2.0(c)										
C D F	4.5(b) 5.7(c)							118-150(b)			55(b)
HEPTANE INSOLUBLE 98°C											
ME - FE	90.5	2.10	7.7					124-164	116		
HÜLS	<96		8.9	9.8	538	58		123-163			83
NESTE-OY	90.5		8.2		404	36		122-162			95
CHALMERS T.H.	86.8	2.10	7.3*		337	35		122-159			
SOLVAY	88.4		6.0	7.2				124-141-165	111		94
D S M	92.0	2.08		8.4	390	33		123-163	106-123		107
UNILEVER	86.6		9.0								
C D F	89.8							124-165			86

* $\%(CH_2)n \geqslant 5$

TABLE 5

SAMPLE EP COPOLYMER (SAGA)HEPTANE SOLUBLE:SOL.98°C(a); INSOL.25°C(b); SOL. 25°C(c)

LABORATORY	wt%	η_{TCB} 135°C dl/gr	IR wt% C_2	NMR wt% C_2	GPC $\overline{Mw}$ 10^{-3}	GPC $\overline{Mn}$ 10^{-3}	L.S. $\overline{Mw}$ 10^{-3}	DSC Tm_1B Tm_2B °C	DSC Tc °C	DSC Tg °C	DSC δH J/g
ME - FE	3.1(b) 7.4(c)	0.57(b) 1.23(c)	15(b) 30(c)					116-136(b) 50-108(b)	102.5 (b) 102.5 (c)		
HÜLS	5.9(c) 6.4(c)		27(c)		131(EP) (c)	9.9(EP) (c)		54-109(c)		-25(c) -36(c)	
NESTE-OY	12.2(a)		23(a)		162(a)			119-158(a)			14.6 (a)
CHALMERS T.H.	3.0(b) 8.6(c)		17.5*					51-109(c) 119-157(c)			
SOLVAY	15.3(b) 9.0(c)		5.0(b) 37.0(c)	4.5(b) 27.7(c)				125-163(b) 51-121 (c)	111(b) 109(b) 86-24(c)	-47(c) -24(c)	93(b) 6(c)
D S M	4.3(b) 6.5(c)	1.04(b) 1.33(c)		11.8(b) 22.9(c)	195(PP) (b) 240(PP) (c)	15(PP) (b) 22(PP) (c)		125-162(b)	112(b) 122(b)	-50(b) -5 (b) -56(c) -8 (c)	85(b)
UNILEVER	10.7(a) 1.8(c)										
HEPTANE INSOLUBLE 98°C											
ME - FE	89.5	2.25	5					122-163	114.5		
HÜLS	<94		6.7	6.5	472	104		124-163			81
NESTE-OY	87.8		4.8		340	52		121-161			
CHALMERS T.H.	88.4	2.12	3.7*		475	67		123-161			
SOLVAY	73.3		2.0	4.6				123-165	113	-8 +7	90
D S M	89.2	2.10		5.23	450	70			123		103
UNILEVER	87.5		5.6					163			

* $\%(CH_2)_n \geq 5$

4. DISCUSSION OF THE RESULTS

(4.1.) Comparison of the fractionation methods

Determination of xylene soluble and insoluble fractions and subsequent structural characterization proved to be a reliable investigation method both qualitatively and quantitatively. By this method, in fact, the amorphous-essentially elastomeric fraction - was separated.
On the other hand, fractionation by hot extraction with heptane on films and subsequent cold separation of the soluble fraction gave less reproducible results. In addition, partially isotactic fractions are extracted; these are only cold separable with difficulty. C_3 crystallinity thus results in the cold soluble fraction, too.

(4.2.) Comparison of the analytical results

Results of intrinsic viscosity were reproducible in these interlaboratory measurements, and the NMR data of wt % C_2 results were also reliable; it was not the case for the corresponding I.R. results. (This technique must be applied only to routine analysis on homogeneous sets of samples).
Values obtained by DSC were comparable enough, provided that uniform heating and cooling conditions were respected.
Homogeneity of the GPC results is adequate, obviously under the same calibration conditions. On the contrary, light scattering results were considerably different confirming the extreme delicacy of this method.

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APPENDIX 1

MICROSTRUCTURE (NMR)

a) DSM RESULTS

SAMPLE	weight % ethylene Total	as PEP	as PEEP	as $P(E)_n P$ $n \geq 3$
Saga original sample	6.9	1.2	1.0	4.7
Xylene ins. 25°C	4.0	0.3	0	3.7
Xylene sol. 25°C	32.8	6.7	7.0	19.1
Heptane extracted film	5.3	1.0	0.6	3.7
Heptane extract 98°, insol.25°C	11.8	0.4	0	11.4
Heptane extract, soluble 25°C	22.9	5.1	6.3	11.5
DSM original sample	8.7	0.5	0.4	7.8
Xylene ins. 25°C	7.6	0.3	0	7.3
Xylene sol. 25°C	46.5	6.6	8.5	31.4
Heptane extracted film	8.4	0	0.7	7.7
Heptane extract 98°C, insol. 25°C	22	0	0	22
Heptane extract, soluble 25°C	34.2	4.6	6.2	23.4

APPENDIX I (contd.)

b) SOLVAY RESULTS

SAMPLE	weight % ethylene Total	as PEP	as PEEP	as $P(E)_nP$ $n \geq 3$
Saga original sample	6.8	1.5	0.7	4.6
Xylene insol. 25°C	2.9	0.4	0	2.5
Xylene sol. 25°C	30.4	9.6	5.3	15.5
Heptane extracted film	4.6	1.1	0.2	3.3
Heptane extract, 98°C, ins. 25°C	4.5	0.5	0	4.0
Heptane extract, sol. 25°C	27.7	8.3	4.6	14.8
DSM original sample	8.6	0.8	0.7	7.1
Xylene insol. 25°C	4.5	0.3	0.3	3.9
Xylene soluble 25°C	41.7	9.7	6.9	25.1
Heptane extracted film	7.2	0.6	0.4	6.2
Heptane extract, 98°C, ins. 25°C	16.9	0.9	0.7	15.3
Heptane extract, sol. 25°C	31.5	5.9	4.5	21.1