Thermodynamic properties and unperturbed chain dimensions of ethylene–propylene copolymers

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An ethylene–propylene copolymer (EPR) of remarkable homogeneity of composition and molecular structure was separated into many fractions, showing very sharp molecular weight distributions (*MWD*), using a recently described method. Phase equilibrium studies were performed on some of these fractions in order to determine, according to Flory's theory, the θ conditions of the copolymer (solvent and temperature). In these conditions, a relationship between limiting viscosity number $[\eta]$ and molecular weight was used in order to ascertain agreement with the 0.5 exponent proposed by theory. The K_θ coefficient, related to the unperturbed dimensions $(\bar{r}_0^2/M)^{1/2}$ and their dependence on temperature, i.e. $(\mathrm{d}\ln\bar{r}_0^2/\mathrm{d}T)$, of the macromolecular chain, were also determined. Furthermore, the very sharp composition and *MWD* of the fractions allowed us to ascertain good agreement between experimental data and Scholte's assumption for the evaluation of molecular weights of EPR and linear low density polyethylene copolymers using size exclusion chromatography.

(Keywords: ethylene–propylene copolymer; molecular weight determination; viscometry; size exclusion chromatography; θ conditions; good solvents; unperturbed dimensions)

INTRODUCTION

It is well known that the performance and final applications of polymeric materials are strongly dependent on their molecular weight and structure. Therefore, in the case of copolymeric systems, great importance is attached to some structural parameters of the chain. In particular, the distribution of comonomeric units, both in the single chain or in different chains, and configurational variations of sequences constitute very important features to be taken into account. Clearly, this complicated situation hinders accurate molecular characterization due to unavoidable overlap of the different contributions. In many cases, this may be responsible for the conflicting conclusions drawn for average values of the raw materials, which may therefore be unreliable.

A methodology which allows the conversion of an experimental chromatogram to a distribution function of molecular weights (*MWD*) was recently proposed by Scholte *et al.*[1] for molecular characterization of ethylene–propylene copolymer (EPR) and linear low density polyethylene (LLDPE) using size exclusion chromatography (s.e.c.). This approach rests upon the assumption that very short side branches of linear macromolecules do not affect the conformations of the skeletal backbone and, consequently, the molecular dimensions on which the s.e.c. separation mechanism is based.

In this work conformational studies on narrow fractions of an EPR copolymer are reported in order to verify Scholte's proposal. The choice of an EPR with a remarkable composition homogeneity is fundamental because the fractionation depends in this case on the molecular weight. On the other hand, the paraffinic nature of the copolymer chain makes the difference in the specific interactions of the comonomers negligible.

EXPERIMENTAL

Sample

The EPR sample used in this study was a commercial product supplied by Dutral S.p.A. The high homogeneity in the comonomer distribution and ratio (propylene content $= C_3 = 53 \pm 2$ wt%) has been shown by fractionation according to molecular weight. The average molecular weight and *MWD* are related to the limiting viscosity number $[\eta] = 1.65$ dl g^{-1} in *o*-dichlorobenzene (ODCB) at 135°C and to a $\bar{M}_w/\bar{M}_n = 2.5$ ratio determined by s.e.c.

Fractionation method

The fractionation method used has been recently described[2]. In addition other results, previously obtained in our laboratory on sharp EPR fractions prepared with solvent gradients, were also considered[3,4].

Viscometric measurements

The evaluation of $[\eta]$ of the fractions and of the raw material was carried out in various solvents and at different temperatures with modified Desreux–Bischoff viscometers[5], designed to make the kinetic energy correction negligible. Every $[\eta]$ value was obtained by extrapolating to $c = 0$ measurements performed at five different concentrations according to Huggins and Kraemer relationships[6,7].

Size exclusion chromatography

The average molecular weight and *MWD* of the fractions and raw material were performed by s.e.c. analysis. A Waters 150 C ALC/GPC instrument, equipped with a set of four 10 μ PL gel columns (10^3, 10^4, 10^5

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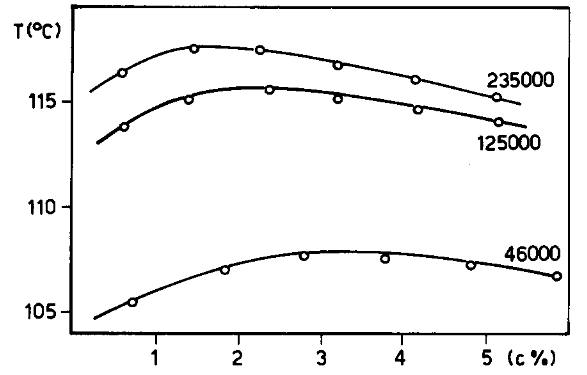

Figure 1 Phase diagram for three fractions of EPR of known molecular weight

and 10^6 Å) and a refractive index detector, was used. The measurements were carried out in ODCB at 135°C; the choice of solvent was decided by the similar value of d*n*/d*c* for the two homopolymers in order to eliminate corrections due to possible composition changes[8].

The s.e.c. calibration for linear polyethylene (PE) was deduced from the universal value suggested by Benoit *et al.*[9]; the latter was determined with sharp polystyrene (PS) standards, and the conversion was made according to the following Mark–Houwink relationships:

$$[\eta]=1.183\times10^{-4}M^{0.71}$$

$$[\eta]=4.43\times10^{-4}M^{0.725}$$

valid for PS and PE, respectively, in ODCB at 135°C[10,11].

The molecular weights of the copolymers were calculated according to the relationship:

$$[\eta]=\{1-(1/3)W_3\}^{a+1}K_{\mathrm{PE}}M_v^a$$

where W_3 is the weight fraction of propylene in the copolymer, and K and a are the Mark–Houwink constants of PE[1].

Infra-red analysis

The average compositions of the fractions and raw material were determined by infra-red (i.r.) analysis on a Perkin–Elmer 1800 FTIR spectrometer. A calibration curve based on the 2723 cm^{-1} absorption band was used.

Critical temperature determination

The phase equilibrium diagrams were determined for three fractions in a range of molecular weights as large as possible. The phase separation temperatures were determined, at every chosen concentration, by cooling the polymer solutions in a well-stirred thermostatic cell in which the rate of temperature decrease (0.2°C min^{-1}) was constant and controlled.

Side lighting and a graduated scale placed behind the solution tube facilitated the detection of phase separation, which manifested by blurring the lines of the thermometric scale.

RESULTS AND DISCUSSION

Phase equilibria

As can be inferred from our previous paper[2] on the fractionation of EPR with diphenylmethane (DPhM), the peculiar solution behaviour suggests a 'θ' point very close to the working temperature range.

A commonly suggested method for θ temperature location relies upon Flory's relationship[12]:

$$1/T_c=(1/\theta)[1+(1/\psi_1)(1/M^{1/2}+1/2M)] \qquad (1)$$

where T_c is the critical temperature, i.e. the maximum of the demixing curve, θ is the θ temperature, ψ_1 is the entropic dilution parameter and M the fraction molecular weight.

Three fractions with very sharp *MWD* and in a molecular weight range 45 000–250 000 were chosen. Their phase diagrams are shown in *Figure 1*, and the straight line extrapolation, according to equation (1), is shown in *Figure 2*. In the extrapolation the term $1/2M$ was neglected because of its low influence on the θ temperature location. The extrapolation, reported in *Figure 2*, yields a θ temperature of 128 ± 0.5°C for DPhM.

Accuracy was confirmed, as shown later, by viscometric measurements which provided a 0.5 exponent for the Mark–Houwink relationship. The slope of the straight line in *Figure 2* allowed an evaluation of the entropic parameter ψ_1 ($\sim$0.53).

Conformations of the copolymer macromolecules

It is well known that $[\eta]$ in θ conditions is related to the macromolecular conformations by Flory's relationship[12]:

$$[\eta]_\theta=K_\theta M^{1/2} \qquad (2)$$

where

$$K_\theta=\Phi(\bar{r}_0^2/M)^{3/2} \qquad (3)$$

where Φ is a universal hydrodynamic constant and $(\bar{r}_0^2)^{3/2}$ the unperturbed dimensions of the specific chain.

Figure 3 shows the $[\eta]$–M relationship for DPhM at 128°C. Extrapolation of the data agrees with the following equation:

$$[\eta]=2.08\times10^{-3}M^{0.5}$$

for which a 0.5 exponent can be found, in good agreement with the theoretical value required by equation (2).

By choosing[13] $\Phi=2.48\times10^{21}$, for the hydrodynamic constant according to the dimensions of $[\eta]$, equation (3) gives:

$$(\bar{r}_0^2/M)^{1/2}=940\times10^{-11}$$

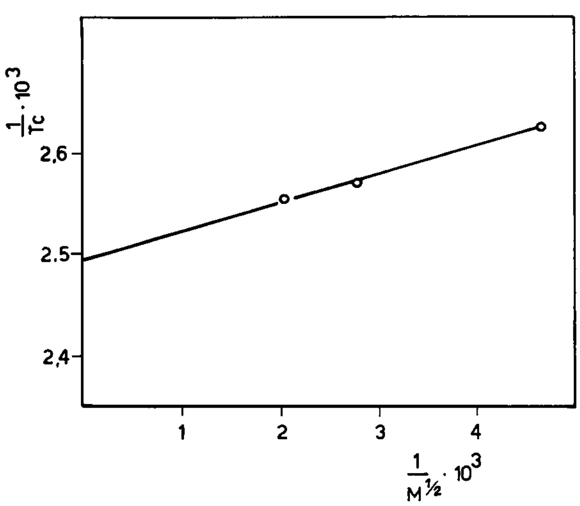

Figure 2 Plot of $1/T_c$ *versus* molecular weight according to equation (1) in DPhM at 128°C

where $\bar{r}_0^2$ (in cm^2) represents the average square end-to-end distance of the unperturbed chain for EPR of $C_3 \approx 50$ wt% at 128°C.

The same conformational parameters can be evaluated by intrinsic viscosity measurements in good solvents[13–17]. Many relationships have been previously suggested and their confidence limits extensively reviewed by Yamakawa[18]. Taking into account the reported suggestions, the Kurata–Stockmayer–Roig (KSR) approach proves to be the most reliable in fitting our experimental data.

Consequently, according to the relationship:

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363\Phi_\theta B\{g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}\} \quad (4)$$

where α_η is the expansion coefficient of the linear macromolecule and

$$g(\alpha_\eta) = 8\alpha_\eta^3/(3\alpha_\eta^2+1)^{3/2} \quad (5)$$

a K_θ value can be obtained through an iterative procedure. The treatment of the data in *Table 1*, according to equations (4) and (5), is shown in *Figure 4*. The K_θ value, calculated from $[\eta]$ in ODCB at 135°C and molecular weights evaluated according to Scholte's method, is in good agreement with the K_θ value determined at 128°C in DPhM, i.e. in pseudo-ideal conditions. In *Figure 4* the latter is a horizontal straight line in agreement with theory.

It is interesting to compare the K_θ values with other previous data in which molecular weights were determined with an absolute method (membrane osmometry)[3] and to study how their trends correlate with those of the homopolymers PE and polypropylene (PP)[19–21].

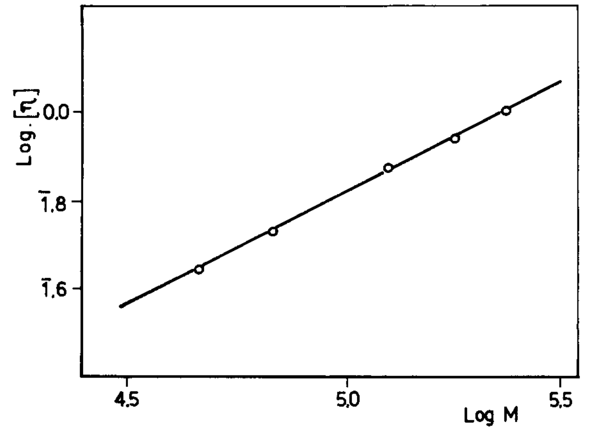

Figure 3 Limiting viscosity number of EPR *versus* molecular weight in DPhM at 128°C

In *Table 2* all previous and actual data for the K_θ values, computed through relationships (2) or (4) and (5) for EPR copolymers with $C_3 \approx 50$ wt%, are given. The K_θ values obtained both in θ and in good solvents are consistent between themselves and with values reported for the homopolymers PE and PP (*Figure 5*).

All these arguments give strong support to the validity of Scholte's assumption[1], in computing the EPR molecular weights. This is not surprising on the basis of other results reported on different polyolefins as shown in *Table 3*. As can be seen, at room temperature, all these data[22–24] are strictly consistent with an average value of

$$(\bar{r}_0^2/x)^{1/2} = 603 \times 10^{-10} \pm 7$$

where x is the degree of polymerization, and with the ratio:

$$(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2} = 1.97 \pm 0.04$$

where $(\bar{r}_{0f}^2)^{1/2}$ represents the average square end-to-end distance of the freely rotating chain[25].

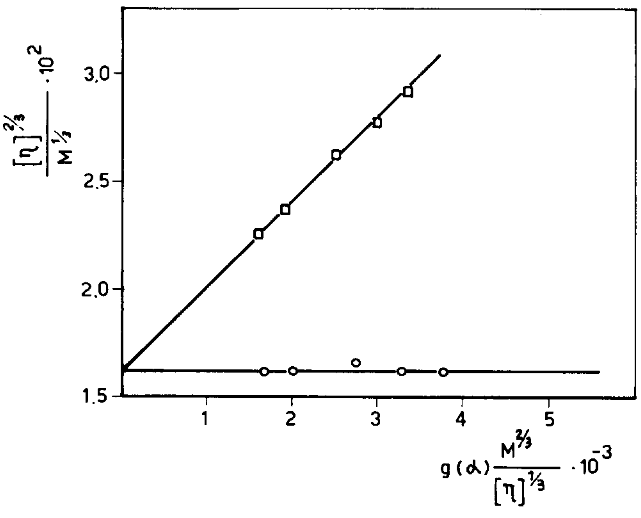

Figure 4 Treatment of $[\eta]$ in ODCB at 135°C (□) and in DPhM at 128°C (○) according to KSR equations

Table 2 K_θ values obtained from various solvents for EPR of $C_3 \approx 50$ wt%

Solvent	T (°C)	$K_\theta \times 10^3$(dl g^{-1})
Cyclohexane	30	2.85
Phenetole	79	2.18
DPhM	128	2.08
Tetrahydronaphthalene	130	2.14
ODCB	135	2.08

Table 1 Limiting viscosity numbers and molecular weights of EPR fractions

Fraction no.	ODCB (135°C) $[\eta]$ (dl g^{-1})	ODCB (135°C) k^1	DPhM (128°C) $[\eta]$ (dl g^{-1})	DPhM (128°C) k^1	$\bar{M}_w (\times 10^{-3})^a$	C_3 (wt%)
1	2.40	0.48	1.00	0.96	235	53
2	1.95	0.40	0.88	0.89	180	53
3	1.50	0.45	0.76	0.78	125	53
4	0.95	0.40	0.54	0.70	68	54
5	0.73	0.38	0.44	0.63	46	54

[a] $\bar{M}_w$ values were computed according to Scholte's proposal

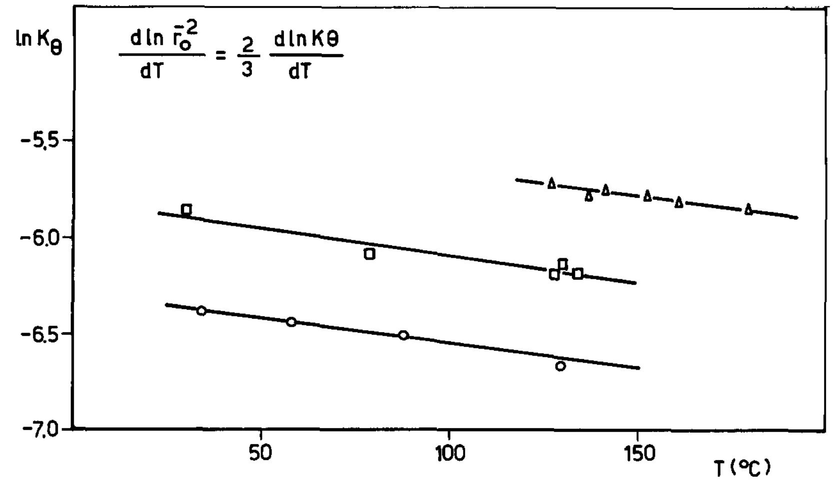

Figure 5 Plot of ln K_θ *versus* temperature of EPR ($C_3 \approx 50$wt%) (□), PE (△) and PP (○)

Table 3 Conformational parameters of some polyolefine backbones with short side chains

Sample	$(\bar{r}_0^2/x)^{1/2}\times 10^{10}$	$(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2}$	Reference
PP	603	1.96	24
Polybutene	609	1.97	23
Polyisobutene	596	1.93	22
EPR (≈ 50wt%)	603	1.97	This work

Dependence of the conformation on temperature

The data for K_θ or $(\bar{r}_0^2/M)^{1/2}$ obtained here in a pseudo-ideal solvent (i.e. DPhM at 128°C) and in good solvent (i.e. ODCB at 135°C) agree very well with the previously reported data where average molecular weights were determined[3] by an absolute method (membrane osmometry). *Figure 5* summarizes all the experimental results for EPR with $C_3 \approx 50$wt%, at various temperatures, in comparison with the trends of the two homopolymers.

It is interesting to notice that a roughly linear dependence on temperature of the macromolecular conformations can be deduced for the copolymer:

$$d\ln \bar{r}_0^2/dT \times 10^3 = -1.8 \pm 0.2$$

As can be seen in *Figure 5*, the displacement of the EPR straight line and its dependence on temperature is in good agreement with the results for the two homopolymers (PE $= -1.78 \times 10^{-3}$ and PP $= -1.8 \times 10^{-3}$)[19–21] according to its composition.

CONCLUSIONS

The results obtained from conformational studies performed on EPR copolymers showing a good homogeneity in composition and molecular structure allowed us to prove the validity of Scholte's assumption that very short side branching of the main chain does not noticeably affect macromolecular dimensions and their dependence on temperature.

To this end the evaluation of $(\bar{r}_0^2/M)^{1/2}$ was carried out on an homogeneous EPR copolymer and a comparison was made with the parent homopolymers. Further evidence was also provided by the agreement of the unperturbed end-to-end temperature coefficient.

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