



Predicting experimental results for polyethylene by computer simulation

J. Ramos, J.F. Vega, J. Martínez-Salazar*

BIOPHYM, Department of Macromolecular Physics, Instituto de Estructura de la Materia, IEM-CSIC, C/ Serrano 113 bis, 28006 Madrid, Spain



ARTICLE INFO

Keywords:

Polyethylene
Molecular architecture
Branching
Dynamics
Crystallization
Computer simulations

ABSTRACT

This feature article reviews several aspects of computational approaches to polyethylene melt and solid state properties in relation to existing experimental results. Based on 40 years of experience in the field, we offer a personal view of how computer simulations are helping to understand the physics of polyethylene as a model polymer. The first issue discussed is the molten state of polyethylene, including static and dynamic properties and entanglement features along with their impacts on rheological behaviour. We then examine the glass transition, crystallization process and solid state structure, including the interlamellar region. This is followed by brief descriptions of the latest advances in simulating mechanical properties and of the various methodologies used to simulate the physics of polyethylene. Throughout the manuscript, references are made to our own work and also to studies by many other authors that have nicely contributed to developments in simulating the physics of polyethylene in close agreement with experimental results.

1. Introduction

Polyethylene [abbreviated PE; IUPAC name polyethylene or poly(methylene)] is the most common plastic, its global annual production being around 82 millions of tonnes [1]. Many kinds of PE are known and these generally consist of a mixture of similar polymers of ethylene.

With regards to polymer physics, PE is undoubtedly the most studied polymer. The reasons for this are its chemical simplicity, its high level of production in the last 50 years and the availability of model materials obtained by different synthetic routes (long chain paraffins [2], single-site catalyst PE that include modelling reactions [2–21] and hydrogenated polybutadienes [22–24]). In addition, architecture is generally well characterized. This has meant that to a greater or lesser extent, the study of PE in the melt or solution, its solid state structure, morphology or physical properties have been the target of the polymer community for over five decades.

There are many types of PE depending on the polymerization procedure used to generate the polymer, and there are also different classifications based on their density.

However, from a strictly physical point of view, several main factors control the physical properties of PE and these are the focus of interest of this article. In this regard, we recognize that the role of branches is a key factor. In this article, we consider PE as the large family of polymers that have the monomer ethylene $-(CH_2-CH_2)-$ as their main constituent, and several side branches which can be classified as long or short. Long chain branching (LCB) in PE is used to describe the presence of side branches whose molecular weight (M_w) is above the critical

molecular weight between entanglements (M_e) but that are not as long as the main chain [25–28]. By short chain branching (SCB), we understand the presence of side branches of up to 6 carbon atoms (1-octene comonomer), and this is a feature of commercially available PE. In between, we find architectures with branches of M_w below M_e . We also consider that branches are randomly placed along the main backbone. In this context, it should be noted that SCB is important for crystallization and solid state properties, while LCB is a determinant of rheological properties with impacts on processing.

As a third point, we should emphasize that several theories of polymers have been applied to PE. Crystal growth theories, crystallographic distortions and mechanical properties are generally applicable but many basic questions still remain unanswered. It should also be considered that the framework of theory describing the molten state and its dynamics is better understood than the solid state properties of PE when compared with model experimental data. Thus, while the selection of experimental results should be filtered according to the complexity of the molecular architecture of the systems, in this paper we have only focussed on experimental results for PE whose molecular architecture has been well characterized.

The points discussed above become important when we try to interpret experimental observations in PE using computer simulation techniques. Here, we review some aspects of computational approaches to PE melt and solid state properties in connection with the available experimental results. Several excellent books and reviews exist on polymer simulations and modelling where the reader can find very valuable information [29–38]. The aim of this feature article is to offer

* Corresponding author.

E-mail address: j.msalazar@csic.es (J. Martínez-Salazar).

our vision of how computer simulations can help in understanding the physics of PE as a model polymer based on our 40 years of experience in the field. The article is organized into four main sections: first we examine the molten state including static and dynamic properties, entanglement features and their effects on rheological properties; next, we discuss the glass transition state, crystallization process and solid state structure, including the interlamellar phase; this is followed by a brief description of the latest advances in the simulation of mechanical properties; and finally we present another brief description, this time of the various methodologies used to simulate the physics of PE.

2. Polyethylene melts: Effect of molecular architecture

The static and dynamic properties of the melt of unentangled or entangled linear, long- or short-branched (LCB and SCB, respectively), or cyclic PE are currently under intense investigation by computer simulations, both using Monte Carlo (MC) and/or atomistic and coarse-graining (CG) molecular dynamic (MD) models (see Section 4.2 for a description of these techniques).

A key component of MC and MD simulations is the description of interactions among atoms and of movements relative to each other. These interactions are described by the so-called “force field” (FF). A broad variety of FFs can be found in the literature applied to n-alkanes and polyolefins (see Section 4.2.5).

In general, all-atom or explicit hydrogen FFs have been used to simulate short alkane properties and, in some cases, to validate united atoms (UA) models [39–42]. However, the presence of explicit hydrogen atoms increases the computational cost of the calculations for long chains, to such an extent that the relevant time- and length-scales in the melt state are out of the reach of current computer capabilities. Notwithstanding, the most widely used for long chains are united atom FFs: (i) OPLS-UA [43]; (ii) SKS-UA [44,45]; (iii) PYS-UA [40,46]; (iv) HMT-UA [47,48]; (v) NERD-UA [49]; (vi) TraPPE-UA [50,51] (vii) GROMOS-UA [52] and (viii) KMT-UA [53]. The description and abbreviations of these force fields are given in Section 4.2.5.

2.1. Volumetric and conformational properties

2.1.1. Volumetric and thermal expansion coefficients

Density, ρ , and its change as a function of temperature is a fundamental property of polymers. The value of ρ is very sensitive to the free volume in the polymer medium. Therefore, the volume-temperature relationship at the pressure of interest must be realistically represented in the simulations. Commonly, ρ , or its inverse, the specific volume, ν , is measured as a function of pressure and temperature using the technique of dilatometry, and it is often referred to as pressure-volume-temperature (PVT) behaviour. There are few PVT results in the literature, mostly for n-alkanes, hydrogenated polybutadienes (HPB), Ziegler-Natta and single-site linear high (HDPE) and linear low density polyethylene (LLDPE) [54–56].

In Fig. 1A, we provide the values of ρ obtained for different chain lengths at a temperature $T \sim 450$ K from different sources, both experiments and simulations [54–57]. MC and MD simulations using both TraPPE-UA and KMT-UA FFs offer an excellent description of both the densities and thermal expansion coefficients of n-alkanes and PE for a broad range of chain lengths and temperatures. HMT-UA also describes the density-chain length dependence, but slightly overestimates absolute values at a given chain length [58]. In the case of the results obtained at $T \sim 509$ K (data not shown), the scattering of simulated data is more pronounced, especially for results obtained using the PYS-UA FF. In effect, this FF tends to overestimate density [59,60] in comparison with experiments and computer simulations performed with OPLS-UA [61], KMT-UA [53,62–65] or TraPPE-UA [66–74] FFs.

Less attention has been paid to the effect of molecular architecture on volumetric properties obtained through computer simulations. Karayiannis et al. reported MC simulation of H-shaped molecular

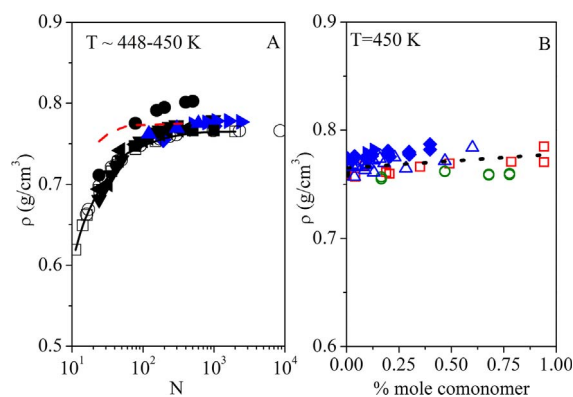


Fig. 1. (A) Comparing the effects of density on chain length dependence for PE at $T = 448\text{--}450$ K in experiments (open symbols and solid line) and in computer simulations (solid symbols): (□) Dee et al. [55]; (○) Pearson et al. [57] (data were obtained from the fit of melt rheological properties to the Rouse and reptation models using RIS calculations for the chain dimensions); (●) MC (HMT-UA) Mavrantzas et al. 1999 [58]; (■) MC (KMT-UA) Karayiannis et al. 2002 [53,62]; (▲) MC (TraPPE-UA) Peristeras et al. 2005 [66]; (▼) MC (KMT-UA) Foteinopoulou et al. [63,64]; (◆) MD (TraPPE-UA) Ramos et al. [69–74]; (◀) MD (KMT-UA) Tsolou et al. [65]; (▶) MC (TraPPE-UA) Baig et al. [67,68]. Dashed red line represents the results of simulations of ring PEs by Tsolou et al. [65]. (B) Calculated densities at 450 K and atmospheric pressure for linear PE and copolymers: (◆) MC (TraPPE-UA) by Ramos et al. and Moorthi et al. [69,71] and experimental densities for (■) linear PE, (○) EP copolymers; (□) EB copolymers and (△) longer ZN and single-site copolymers by Han et al. [56] at $T = 450$ K as a function of comonomer mole fraction. The dashed black line is an eye-guide line for the experimental values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

architectures in PE using their KMT-UA model [75,76]. Tsolou et al. did the same for ring PE systems [65]. Interestingly, these authors found that ring PE melts reach the asymptotic regime (where no variation of ρ with molecular length is observed) at lower N values than the corresponding linear PE melts (dashed red line in Fig. 1A). This observation was attributed to the absence of chain ends in rings, the density of the rings being always higher than that of the corresponding linear systems of similar molecular weight. These cyclic structures were also examined by Hur et al. through MD simulation using PYS-UA and SKS-UA non-bonded parameters FF at $T = 509$ K [59]. The results obtained for ρ as a function of molecular length are in qualitative agreement with those obtained by Tsolou et al. [65].

Peristeras et al. assessed the volumetric properties of tri-arm star PEs by MC simulations and TraPPE-UA FF [66]. These authors reported good agreement between their MC simulations and the experimental ρ values for low density polyethylene (LDPE). Baig et al. also examined H-shaped, pom-pom and SCB PE melts by MC simulation using TraPPE-UA FF [67,68]. In a systematic way, Ramos et al. explored the effects of different amounts and types of SCB (from 1-butene to 1-decene) by MC and MD also using TraPPE-UA FF [69,71]. In all these studies, the simulated values of ρ slightly increased with the comonomer mole fraction, in agreement with the experimental results reported for different polyolefins [54–56], as can be observed in Fig. 1B.

The thermal expansion coefficient at constant pressure, α , has been also analyzed by some authors. However, results so far are much more limited. From the specific volume data (\bar{V}) at different temperatures, α is defined as:

$$\alpha = -\frac{1}{\bar{V}} \left(\frac{d\bar{V}}{dT} \right)_p = \left(\frac{d \ln \bar{V}}{dT} \right)_p \quad (1)$$

In general, simulations using KMT-UA, OPLS-UA and TraPPE-UA FFs show particularly good agreement with experiments, including a decrease in α with molecular length up to values of around $6.6\text{--}6.9 \times 10^4 \text{ K}^{-1}$ (KMT-UA) [53,62,64], $7.6 \times 10^4 \text{ K}^{-1}$ (OPLS-UA) [61] and $8.6 \times 10^4 \text{ K}^{-1}$ (TraPPE-UA) [73]. For linear high molecular weight PE, experimental values vary between $7.6 \times 10^4 \text{ K}^{-1}$ and

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