



# INFLUENCE OF BRANCH CONTENT OF ETHYLENE/1- HEXENE METALLOCENE –BASED LLDPE ON ITS MISCIBILITY WITH LDPE: A MOLECULAR DYNAMICS STUDY

Tayyab Hameed<sup>1</sup>, Basel F. Abu-Sharkh<sup>2</sup>, Ibelwaleed A. Hussein<sup>3</sup>

1: Graduate Student, Chemical Engineering Department, KFUPM, Dhahran 31261.

2: Associate Professor

3: Assistant Professor

E-mail: [ihussein@kfupm.edu.sa](mailto:ihussein@kfupm.edu.sa), Fax: +966 3 860 4234

## ABSTRACT

*The effect of branch content of hexene metallocene linear-low-density polyethylene (m-LLDPE) on its miscibility with low-density polyethylene (LDPE) was studied by molecular dynamics simulation. The branches of m-LLDPE were varied from 10 to 80 branches/ 1000 C, distributed uniformly on the chain. The LDPE was modeled as three long-chain branches with 22 short chain branches of different kinds. m-LLDPE and LDPE were blended at 500K and 450K. The results showed complete miscibility of blends for all the branch contents covered in this study. Lamellar structures in the melts of m-LLDPE and LDPE blends were detected up to a branch content of 40/1000 C.*

## INTRODUCTION

Polyethylene is produced in many forms, each of which has different properties resulting from variations in structure. The melting temperature depends on both the molecular constitution and crystallization conditions. High density polyethylene (HDPE) has a linear structure with a peak melting point in the range of  $130^{\circ}\text{C} < T_m < 135^{\circ}\text{C}$ . Low-density polyethylene (LDPE) is produced by free-radical polymerization and contains both long and short-chain branches and has a melting point in the range  $108^{\circ} < T_m < 115^{\circ}\text{C}$ . Linear low-density polyethylene (LLDPE)

is produced by co-polymerizing ethylene with an  $\alpha$ -olefin such as 1-butene, 1-hexane or 1-octene. The melting point of LLDPE is  $<135^{\circ}\text{C}$  and is a strong function of the branch content.

The properties of the individual species can be altered by mixing the components, and blends of HDPE, LDPE and LLDPE are widely used commercially. Polyethylene-polyethylene miscibility has been a topic of great academic and commercial interest for the past decade, owing to its relevancy to the understanding of processing and performance properties of blends containing different types of polyethylenes. Despite considerable efforts that have been made to the subject, a consensus has not yet been achieved concerning the liquid-liquid miscibility of such blends. For example, different groups of researchers have proposed completely opposite views ranging from total phase separation [Barham et al., 1988; Hill et al., 1991; Hill et al., 1992; Barham, 1994] to complete homogeneity [Alamo et al., 1994 and 1997; Agamalian et al., 1999] for HDPE/LDPE blend. Nevertheless, in the case of HDPE/LLDPE blends, researchers have demonstrated unanimously that the average number of branches per thousand carbons (i.e. the branch content) of LLDPE is the major molecular factor that controls miscibility [Hill et al., 1993; Barham et al., 1993; Hill and Barham, 1994; Alamo et al., 1997; Choi, 2000]. Blends of LLDPE and LDPE have received far less attention than HDPE/LDPE and HDPE/LLDPE mixtures with reports ranging from immiscibility to partial miscibility [Utracki, 1989; Muller and Balsamo, 1994; Lee and Denn, 2000; Hussein and Williams, 2001]. The effect of branch distribution in the case of LLDPE is also unresolved. Some researchers [Xu et al., 2002; Zhao et al., 1997; Lee et al., 1997] have shown that blends containing ZN-LLDPE, which has a nonuniform branch distribution, behave differently than m-LLDPE with uniform distribution of braches, which indicates the importance of branch distribution. However, Reichart et al., [1998] reported no effect for branch distribution on the miscibility of HDPE/LLDPE blends using SANS.

While a certain understanding of the miscibility of polyethylenes has been accumulated using the various experimental techniques described in the above references, research on the same subject from molecular modeling point of view has been very little. Maranas et al. [1998;] used MD to calculate cohesive energy density and internal pressure and found that solubility parameters thus computed agreed with the results from SANS experiments from the same group [Grasseley group]. Recently, Choi [2000] and Fan et al. [2002] have studied HDPE/butene-LLDPE and HDPE/LDPE systems by computing solubility parameters,  $\chi$ . The LDPE/m-LLDPE blend system is yet to be studied by MD simulations. Instead of computing the  $\chi$  values, the steady-state conformations for the blend model were generated to explore the effect of branch content of 1-hexene m-LLDPE on its miscibility with LDPE. Similar work was carried out by Choi et al. [1995] for blends of polyethylene/polypropylene.

## **SIMULATION METHODOLOGY**

Five blend models of LDPE/1-hexene m-LLDPE systems were studied. The characteristics of the component models (molecules) are shown in Table 1 in which model 0 corresponds to

LDPE and models 1-5 represent 1-hexene m-LLDPEs with different branch contents. The LDPE molecule was modeled with three long branches composed of 500 carbon atoms and 11 short branches, i.e. the branch content is 25 branches/1000 C (including long and short branches). Note that most of the commercial LDPE products bear 15-30 branches / 1000 C and among the branches there may be 1-3 long branches. In this work, effort was made to construct representative models that are close to commercial products. The LDPE was constructed by arbitrarily attaching a long chain of 100 carbon atoms to a 400-carbon atom chain and then putting the short branches randomly along the three long chain branches. The LLDPE is composed of 500 backbone carbon atoms with a fixed number of branches distributed uniformly along the backbone chain, which resembles the LLDPE produced by metallocene catalysts. In fact, the modeled m-LLDPE are similar to hydrogenated polybutadiene (HPB) rather than commercial m-LLDPE. The HPB were used in the miscibility studies of Alamo et al. (1997). The respective branch content was set at 10, 20, 40, 60 and 80 branches for each LLDPE model. The reason for using long chains rather than short chains (e.g. 100 backbone carbon chains) is to capture the branch content effect with a statistically representative model. Because of the size of the model, a united atom-approach was used to reduce the computational time.

Canonical (i.e. NVT) MD simulations were carried out at 500K for all model blends based upon the scheme developed by Nose [1984] with a Leapfrog numerical algorithm. For all models, the simulation time was 1000 ps ( $10^{-12}$ ) with a time step of 1 fs ( $10^{-15}$ ). In the absence of density constraints, segments composing the chain have more chances to reorient and assume their optimal configurations in a shorter time [Choi et al., 1995]. Integration time step of 0.005 ps and a relaxation constant of 0.1 for the relaxation heat variable bath were applied throughout the simulations. The Dreiding II force field potential was employed [Mayo et al., 1990] because of its simplicity and availability of the united-atom parameters. The geometric and energetic parameters were as described by Mayo et al. [Mayo et al., 1990]. Nonbonded interactions were modeled using a Lennard-Jones potential with a cutoff distance of 10 Å.

Table: 1

Model	Molar mass (g/mol)	Hexene mol %	Branch content; CH <sub>3</sub> /1000C	
			long <sup>a</sup>	short <sup>b</sup>
0 (LDPE)	7518	0	3	25
1	7560	2	0	10
2	8120	4	0	20
3	9240	8	0	40
4	10360	12	0	60
5	11480	16	0	80

<sup>a</sup> Branches containing > 6 carbon atoms. <sup>b</sup> Branches containing ≤ 6 carbon atoms.

## RESULTS AND DISCUSSION

The steady-state conformation for m-LLDPE/LDPE with 10 branches/1000 C is shown in Figure 1. Figure 2 is a side view of the blend of m-LLDPE with 10 branches and LDPE. In all Figures, the magenta line represents LDPE and the gray one is for m-LLDPE with branches colored in red. Chain folding in lamellar structures is evident for both LDPE and m-LLDPE with branch contents of 10, 20, and 40/1000 C as shown in Figures 1, 3 and 4 respectively. Figures 1, 2, 3, and 4 show the mingling of the m-LLDPE and LDPE chains suggesting the miscibility of the two polymers. This mingling and interactions is observed even at high branch contents of 60 and 80 branches/1000 C. Steady-state conformations for the blend with 80 branches/1000 C are shown in Figure 5. These results suggest the miscibility of m-LLDPE

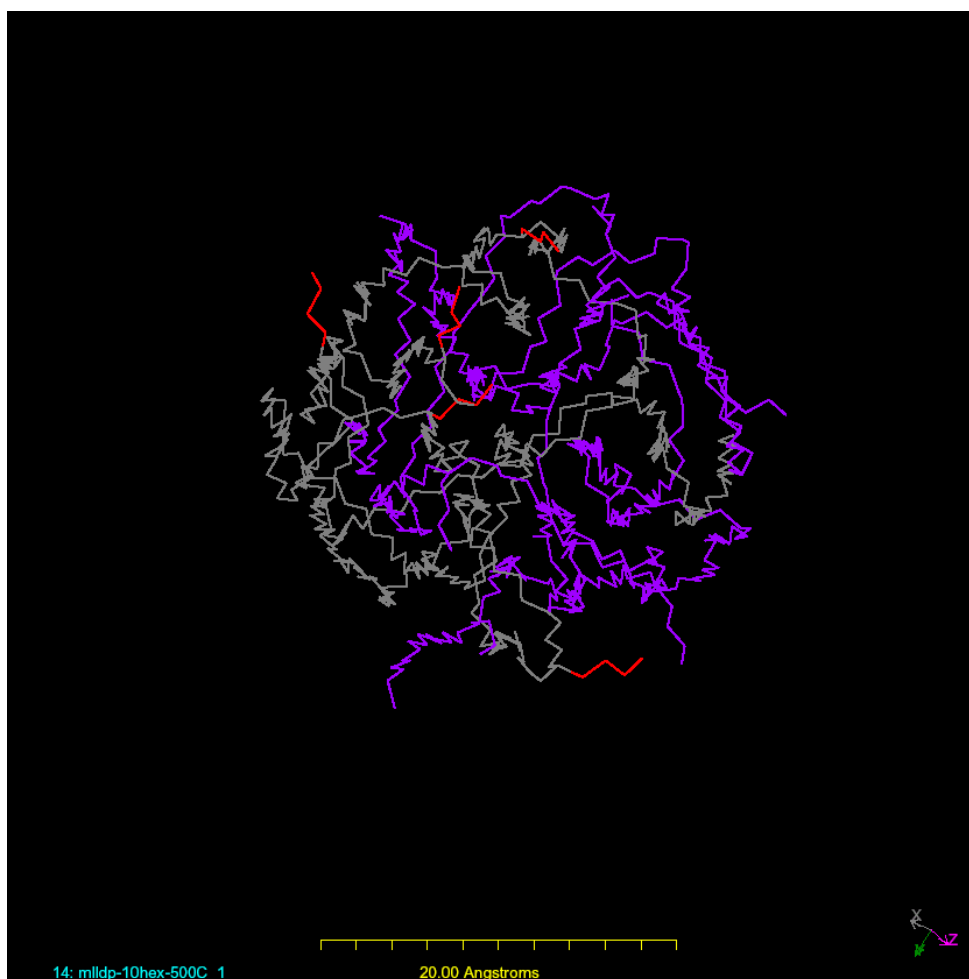


Figure 1: Blend of LDPE/ m-LLDPE with 10 SCB/1000C at 500K

in LDPE in the range up to 80 branches/1000 C. In Figures 1-4, the chain folding of the PE chains suggests the persistence of lamellar structure in melts of m-LLDPE and LDPE almost 100 K above the melting point. The lamellar structure and substantial order in the melt can easily be observed. These observations on order in the melt are in agreement with NMR results of Bremner and Rudin (1992) who reported substantial order in melts of LDPE at 423 K. However, in the last two Figures, increased branching has disturbed the lamellar structure. Overall, the MD simulation results suggest miscibility of m-LLDPE in LDPE model that was used in this study. However, it should be noted that MD simulations resemble 50/50 blends only and do not provide information about the full composition spectrum. In addition, the structure of LDPE may also play a factor on miscibility. MD simulations that look into the effect of the structure and density of long-chain branching on the miscibility are underway.

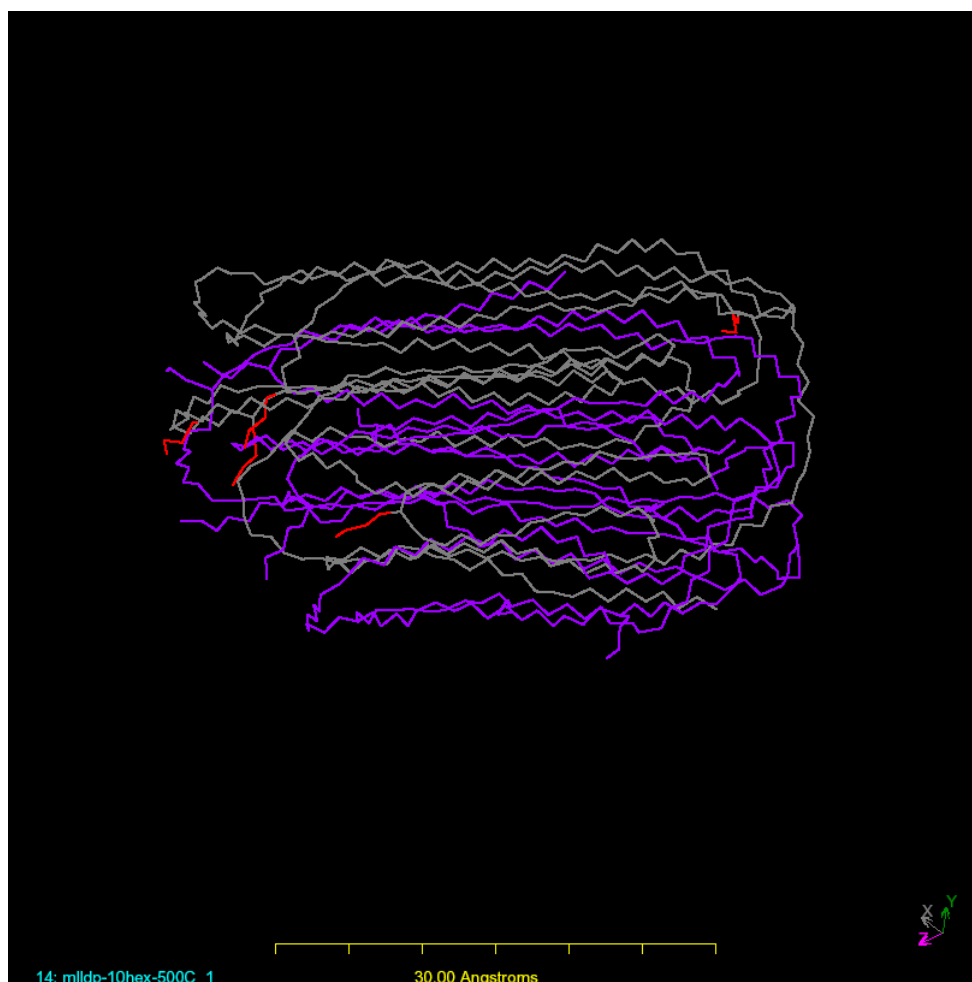


Figure 2: Blend of LDPE/ m-LLDPE with 10 SCB/1000C at 500K, Side View

In addition, experimental study that will use rheology to explore miscibility of the pairs covered in this study as well as further analysis of simulation results will be carried out and reported elsewhere (Hameed, 2002).

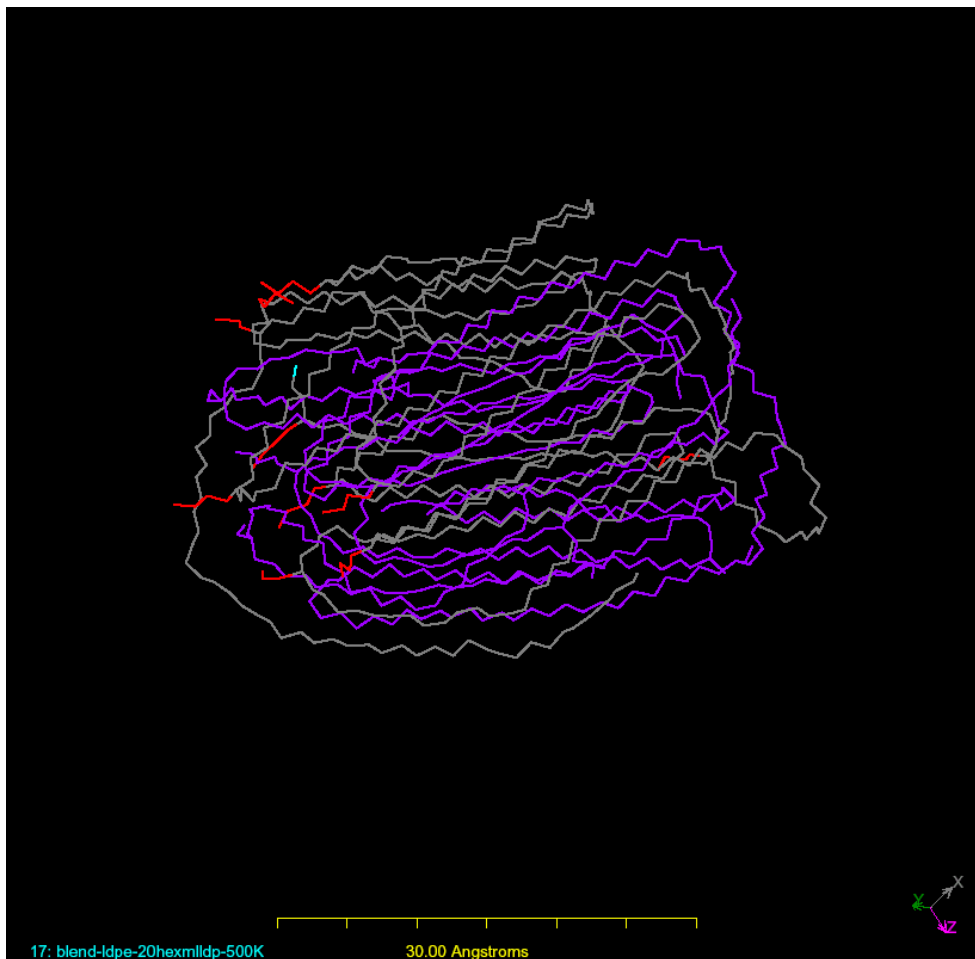


Figure 3: Blend of LDPE/ m-LLDPE with 20 SCB/1000C at 500K

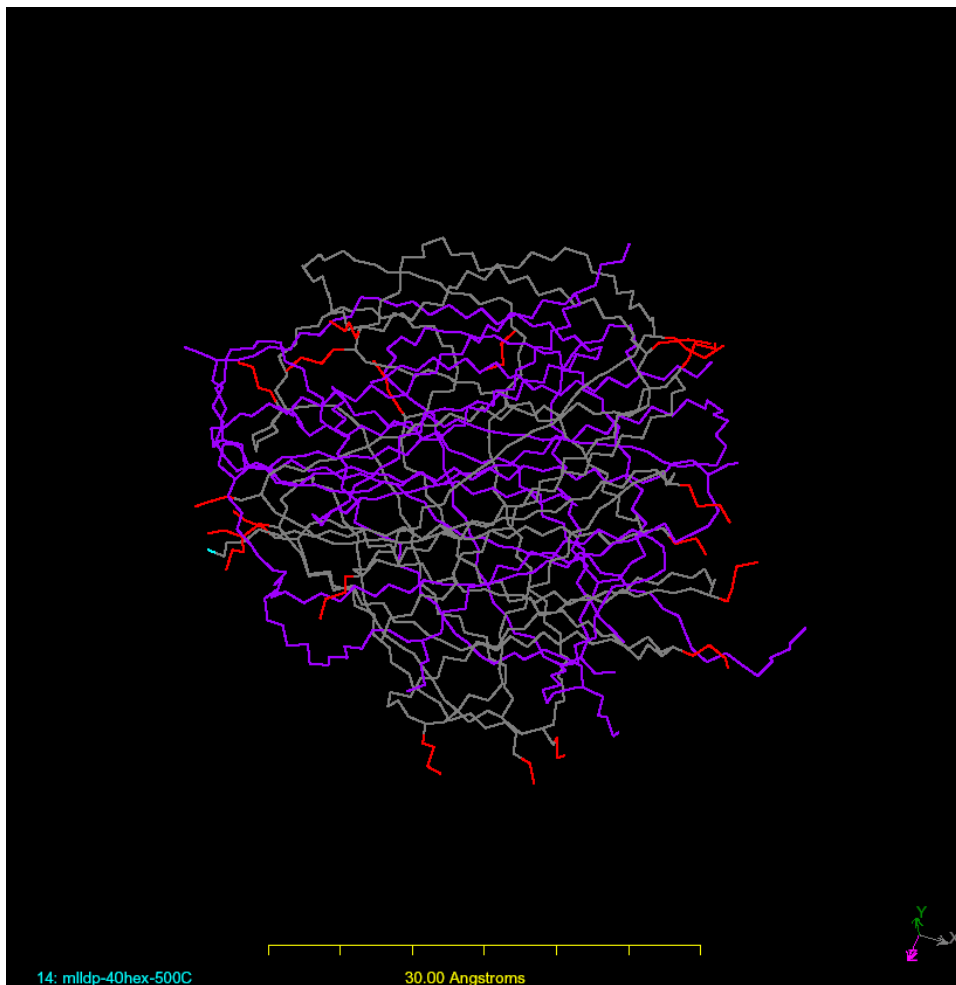


Figure 4: Blend of LDPE/ m-LLDPE with 40 SCB/1000C at 500K

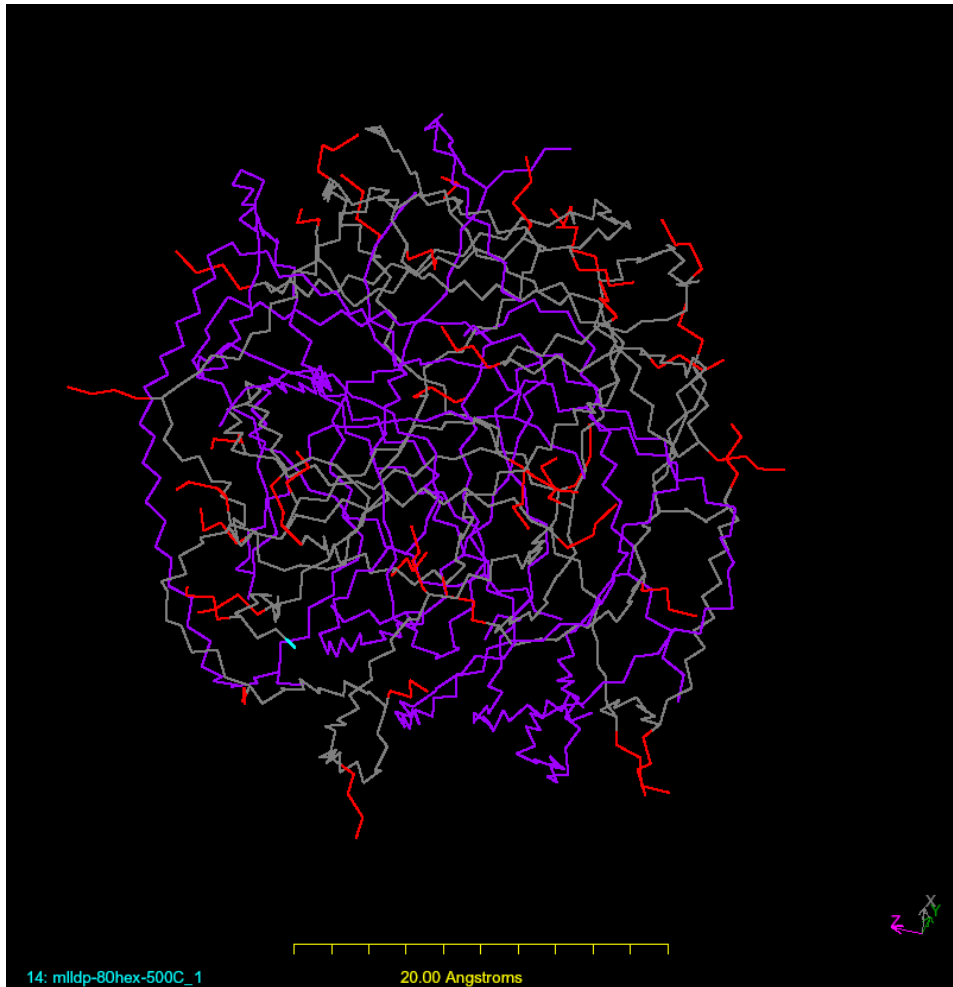


Figure 5: Blend of LDPE/ m-LLDPE with 80 SCB/1000C at 500K

## CONCLUSION

Miscibility of m-LLDPE in LDPE was observed for m-LLDPE with branch content up to 80 branches/1000 C. Lamellar structures in melts of m-LLDPE and LDPE blends were detected up to a branch content of 40 branches/1000 C. Density of lamellar structures was found to be a function of branch content.



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