Investigation of Molecular Structure of LDPE Modified by Itaconic Acid Grafting

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ABSTRACT: Using thermomechanical spectroscopy, the molecular-weight distribution and relaxation transitions have been investigated in commercial LDPE and grafted by itaconic acid (LDPE-g-IA). This grafting in the molten LDPE was done by reactive extrusion with varied content of reactants in the blend under alternating of a shearing rate applied onto the melt. The dependence of structural relaxation changes in LDPE is shown upon the depth of the mechanochemical transformations and the competing reactions at IA grafting, and also on the chemical crosslinking of the macromolecules. The reason for MWD bimodality for LDPE-g-IA obtained in dynamic mixing is the raised homogenization degree of the reactive blend and the higher grafted product yield compared with static mixers. The mixer type substantially affects the structure of the LDPE-g-IA amorphous phase. The data obtained reflect chemical transformations of LDPE molecules in IA's presence without an initiator of radical reactions (DCP). Most probable is the IA initiation of molecular crosslinking reactions. There could also occur IA thermodegradation and oligomerization. LDPE and IA or products of acid chemical transformations do not agree thermodynamically (the calculated solubility parameters are 16.1 (MJ/m³)^{0.5} for polyethylene and 26.4 (MJ/m³)^{0.5} for IA). From the above procedure it can be supposed that nongrafted IA (or its oligomers) exerts an antiplastifying effect on LDPE and LDPE-g-IA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1771-1779, 1999

Key words: LDPE; itaconic acid; dicumyl peroxide; reactive extrusion; static mixer; dynamic mixer; grafting; thermomechanical spectroscopy; molecular-weight distribution; relaxation transition

INTRODUCTION

Grafting of the nonsaturated monomers containing functional groups to olefin polymer mac-

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romolecules aimed to create functional polymers is widely applicable in present-day chemistry, chemical technologies, and polymer materials' science.¹⁻⁸ Functional polymers are intended predominantly to produce polymer blends in which they play the role of modifiers or compatibilizers.⁹ The fundamental characteristic of polymers functionalized by grafting of the olefin monomer is grafting efficiency. So, investigators engaged in the synthesis of functionalized polymers seek to reveal the mecha-

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nism of grafting reactions, which offers control over the grafted product yield.

Most often grafting reactions are performed using reactive extrusion.⁹⁻¹⁴ Here, they are affected by nonstationary heat fields and shear of the moving reactive melt. Both the main reaction of grafting monomer and many side processes (crosslinking and degradation of macromolecules, oligomerization of the grafted monomer, macromolecule crosslinking by the monomer molecules, etc.) can be mechanically and chemically initiated. The mentioned reactions could run simultaneously, so due to their competition, the composition and properties of final product, and its molecular structure can be drastically changed. Owing to this fact, the molecular and topological structures of the grafted polymers should be studied along with the grafting efficiency. This helps to determine and optimize factors contributing to obtain a product with the given properties.

The effect of mixing conditions ensured by the design of static and dynamic mixers on IA grafting to LDPE using reactive extrusion was studied earlier.¹⁵ The present article tries to examine the influence of grafting conditions predetermined by the extruder-reactor design and the reaction system on variations in LDPE molecular and topological structures.

EXPERIMENTAL

Materials and Apparatus

Like in other publications¹⁵ we used a low-density polyethylene produced by the Polimir Co. (Polotsk, Belarus), and itaconic acid from the Chemical Division, Pfizer Inc., New York. Dicumyl peroxide (DCP) produced at AO Kazanorgsintez, Russia, was used as an initiator.

Grafting reactions were accomplished in the laboratory extruder-reactor assembled on Brabender's plastograph base. The method of grafting and description of both the static and dynamic mixer designs are given in another article.¹⁵ The shearing rates (*j*) in the moving reactive melt were 50 and 100 s⁻¹ for the static mixer and 100 s⁻¹ for the dynamic one.

Characterization

The efficiency of IA grafting characterized as the grafted acid weight ratio to its total amount in LDPE was determined by IR-spectroscopy.¹⁵ The

polymer melt viscosity was characterized by the Melt Flow Index (MFI) determined under the same parameters (temperature 190°C, load 10 kg) as in other publications.¹⁵ The results of the grafting efficiency and the melt fluidity in the studied materials are shown in Table I.

Thermomechanical Spectroscopy (TMS)

A detailed description of TMS used is given elsewhere.¹⁶⁻¹⁸ In this article¹⁶ a theoretical basis of calculations of molecular-weight distribution based on the analysis of thermomechanical curves (TMC) is shown. The data on the morphological structure of the LDPE/PA6 blend, relaxation transition temperatures, phase structure of the mixed polymers, and their molecular characteristics are known.¹⁷ In another article,¹⁸ taking as an example the TMC of polybutadiene, the methodology of evaluation the number-average and the weight-average molecular weight was described in details. In the present work as in other articles,^{17, 18} thermomechanical curves were obtained by measuring penetration of a quartz semispherical probe (4 mm in diameter) into the sample. The study was performed by using a UIP-70M device, developed at the Russian Academy of Sciences. The samples for testing were made of LDPE and LDPE-g-IA. They had a form of a cylinder with a diameter of 4-6 mm and a hight of 2-4mm. Tests were done in a dilatometric regime. The analysis was conducted in the temperature range $-150-+150^{\circ}$ C at the temperature scanning rate of 5°C/mm. The methodology of processing the results of measurements, evaluating coefficients of volumetric thermal expansion, and construction molecular-weight distribution curves are cited in other works.^{16–18} The method used to evaluate TMC had a high reproducibility of results. The error of calculated parameters did not exceed 3%, which resulted from a high accuracy of temperature $(\pm 0.05^{\circ}C)$ and deformation $(\pm 0.005\%)$ measurements.

RESULTS AND DISCUSSION

TMC of LDPE

In Figure 1(a) TMC of virgin LDPE is shown. The polymer in the indicated temperature interval has two relaxation transitions (called here glass transitions), which is evidenced by two characteristic temperatures (T_g) . This is the evidence of a presence in the macromolecular structure of two blocks with different molecular mobility. The first

No. of Composition	A Type of Mixer	IA Concentration (wt %)	DCP Concentration (wt %)	Efficiency of Grafting (%)	Melt Flow Index (g/10 min)
1		0	0	0	17.8
2		1	0	0	14.8
3		2	0	0	17.0
4		5	0	0	17.0
5	A static mixer $i = 50 \text{ s}^{-1}$	1	0	0	15.8
6	It static mixer j = 50 5	1	01	62 5	13.3
7		1	0.2	75.2	6.5
8		1	0.3	84.5	2.7
9		2	0.3	65.3	8.0
10		5	0.3	31.2	10.8
11	A static mixer $i = 100 \text{ s}^{-1}$	1	0.0	0	15.0
12	II Static Illixer J 100 S	1	01	44 0	15.5
13		1	0.2	71.0	9.5
14		1	0.3	81.1	4.8
15		2	0.3	77.2	7.3
16		5	0.3	55.1	10.6
17	A dynamic mixer $i = 100 \text{ s}^{-1}$	1	0	0	15.5
18	ri uynamie mixer j 100 s	1	01	77 7	13.6
19		1	0.2	87.0	7.6
20		1	0.3	91.6	4.3

Table I Characteristics of Investigated Materials

relaxation transition from the glassy state to a high elastic one is observed in point *B* and corresponds to $T_{gI} = -50^{\circ}$ C. Above this temperature a



Figure 1 Thermomechanical curve for nonmodified LDPE and a fragment of such a curve for HDPE.

high-elastic deformation of the polymer takes place, accompanied by the high elasticity emergence on the high-elasticity plateau at a temperature in point C. Tangents of the CD slope corresponds to the thermal expansion coefficient of volume (a_2) of polyethylene in a high-elastic region of the low-temperature block.

The second relaxation transfer at the temperature in point E corresponds to defrosting of the high-temperature block, where linear chains in the plateau region of high elasticity are aggregated, being junctions of the physical network of the low-temperature block. The second transition temperature is 82°C. Above this temperature a high elastic expansion of polyethylene with a_3 coefficient occurs up to the temperature in point F. Then the high-elastic thermomechanical deformation takes place again (probe penetration into the polymer). This is attributed to a sequential transition of different molecular weight homolog (from a low-molecular to the highest molecular weight) into "sol" and related reduction of the modulus of the physical network to zero.¹⁶ This moment approaches at a temperature about point G, after which the polymer goes over to the regime of a molecular flow (segment GH of the curve). In Figure 1 the recorded LDPE relaxation

transitions at -50 and 82° C are known.¹⁸ There does not, however, exist any explanation of their origin.

In our opinion, the mentioned relaxation transitions should be attributed to different types of associates (blocks) of macromolecule sites forming an LDPE amorphous phase. In Figure 1, a fragment of TMC for HDPE is also displayed. It has a higher crystallinity degree compared with LDPE. The deformation peak on this curve arising from the melting stage of the polyethylene crystalline part is clearly seen between 115 and 120°C against the viscous flow curve of an HDPE amorphous phase.

LDPE Modified in the Static Mixer

The properties of LDPE compositions produced in static mixers at 50 s⁻¹ and 100s⁻¹ shearing rates are listed in Table II [compositions (5)– (16)]. Here data on materials containing IA introduced into LDPE without applying any substantial shearing force on the melt are also collected [compositions (2)–(4)].

It is obvious from Table II that LDPE having a diblock structure and dominating a low-temperature block (73 wt %) has transformed after introduction of 1wt % of IA by using a static mixer with $j = 50 \text{ s}^{-1}$ into a homogeneous single block polymer [compositions (1) and (5)]. The TMC of the LDPE/IA system characterizes it as a homogeneous polymer with only one relaxation transition at 49°C, the temperature of the beginning of a flow -96° C, and averaged free volume $V_f = 0.258$. LDPE in the low-temperature block had a V_{f1} = 0.102, and in the high-temperature block V_{t2} = 0.313. This characterizes the first block as a typical flexible elastomer, with the second one as a rather rigid and compact pseudocrystalline structure. The disappearance of T_{g1} from the TMC for LDPE/IA 1 wt % (Fig. 2) could be related to the antiplasticization by the nongrafted IA, which should give some limitation of mobility of polyethylene chains.

Introduction of 0.1 wt % of an initiator of grafting a reaction, namely DCP into LDPE with IA at $j = 50 \text{ s}^{-1}$, does not vary much the polymer topological structure (Fig. 2), but negligibly reduces the average molecular weight [Table II, compositions (5) and (6)]. An increase in the concentration of DCP to 0.2 and 0.3% considerably changes the polymer topological structure. From the single block it transforms into the triblock structure with relaxation transitions from the glassy state



Figure 2 Thermomechanical curves for a single [composition (5)] and triblock LDPE [composition (7)].

to the high elastic one at -105 and -3°C for two low-temperature blocks, respectively, and at 43°C for the high-temperature one [Table II, composition (8)]. Comparing LDPE-g-IA [composition (7)] structure with the initial polymer, a LDPE-g-IA low-temperature block has evidently divided in practically equal weight portions into two blocks, whereas the high-temperature structure has retained its initial one, though with a slightly elevated chain flexibility, i.e., its glass transition temperature is dropped from 62–36°C. The observed changes in the polyethylene structure are evidence of processes in chemical reactions leading to varying parameters of the polymer chain. So, it again becomes a multiblock structure with high elastic chains of the low-temperature block.

An increase in the DCP concentration up to 0.3 wt % results in the raised total weight content of the polymer having a rubber-like flexibility of chains. The amount of a rigid structure reduces 1.5 times compared with the initial LDPE [Table II, compositions (1) and (8)]. Note, that because of the IA grafting the molecular weight between junctions in the low-temperature block is reduced noticeably from 6160 of the initial LDPE down to 2980 in LDPE-g-IA, with 0.2 wt % of the DCP concentration and to 830 at 0.3 wt % of the DCP [Table II, compositions (1), (7), and (8)]. This is a result of additional junctions that emerged in the flexible-chain polymer block, which appear to be due to the increased degree of macromolecules crosslinking during the competing processes of the IA grafting and chemical crosslinking of the macromolecules [Table I, compositions (6)–(8)].¹⁵



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6 lg M_i Figure 3 The MWD of LDPE in compositions (1) curve (1), (5) curve (2), and (6) curve (3)-numbers correspond to those cited in Table I. The molecular structure of the high-temperature block also changes with increased initiator

content. Compared to the low-temperature blocks, the growth of \overline{M}_n is observed at the LDPE mixing with either IA alone or IA with DCP. At 0.2 wt % of the DCP concentration, the growth of the molecular weight stabilizes. Calculations of the V_f parameter, which reflects the density of macromolecule packing in the block structure, proves that just at this DCP concentration the polyethylene structure closely approaches the rubber-like one. The values of $V_{f1} = 0.109$ and V_{f2} = 0.115 are characteristic of rubber-like polymers.¹⁹

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Considerable changes at IA grafting are also observed in the shape of molecular weight distribution (MWD) in the LDPE high-temperature block at its modification in a static mixer (j = 50 s^{-1}). In nonmodified polyethylene [Fig. 3, curve (1)] it is unimodal and symmetrical. Here, polydispersity coefficient K approaches equal about 1. For LDPE-g-IA, it noticeably expands (K = 2.15)and MWD becomes bimodal [Fig. 3, curve (2)]. This confirms that the chemical reactions are running between LDPE and IA molecules even without DCP. Bimodal character of MWD is the evidence of complex interactions where thermomechanically initiated reaction creates at least two centers of chain growth of unlike activity, and they are transferred to the polymer. As a result, such behavior gives the chain's ramification and,

consequently, the coefficient of polymer polydispersity rises. Because in DCP absence IA grafting is not observed¹⁵ [Table I, composition (5)] and the melt viscosity increases compared with the initial LDPE [Table II, compositions (1) and (5)], it can be presumed that IA can initiate few crosslinks in LDPE.

Introduction of 0.1 wt % of DCP evidently simplifies the mechanism of reactions. Thus, the molecular structure of the high-temperature block becomes more uniform with unimodal MWD, similar with the previous case of a wide distribution [Fig. 3, curve (3)]).

Increase in a shearing rate in the static mixer from 50 to 100 s^{-1} at the polyethylene mixing with only IA [Tables I and II, composition (11)] preserves the diblock structure of polyethylene with two relaxation transitions at -52 and 29°C compared with low-velocity mixing. Molecular characteristics of the low-temperature block are retained approximately the same as for nonmodified LDPE. A high-temperature block of LDPE shows upon mixing in the given conditions a lower temperature of the relaxation transition, an increased molecular weight of the chain fragments, and a polydispersity coefficient K compared to the initial polymer and LDPE-g-IA produced in a mixer with $j = 50 \text{ s}^{-1}$. These data show that the high-temperature block loosens, evidently because of the raised concentration of branching formed due to the LDPE transformations initiated by IA.

Mixing of LDPE and IA in the presence of 0.1 and 0.2 wt % of DCP fully homogenizes the polymer structure. It shows only one high-temperature relaxation transition at 38 and 46°C, correspondingly [Table II, compositions (12) and (13)]. The molecular weight of the LDPE blocks and its K tends to be reduced. As for the chain rigidity and the packing density characterized by the value of free volume V_{f} , these noticeably increase in compositions (11)–(13), then transform from the almost rubber-like structure into the typical of a rigid plastics one.

At LDPE mixing with IA in the presence of 0.3 wt % of DCP, its topological structure becomes diblock again with relaxation transition temperatures (Table II) at -38 and 41° C. From Table II [compositions (1) and (14)] it is concluded that the number of junctions in the intermolecular network of the low-temperature block reduces almost twofold in contrast to the initial LDPE. Evidently, this is related with the reduced weight share of the high-temperature block (φ) , considerable re-

ameters of Initial and Modified	
e Transitions and Molecular Par	
Temperatures of Structural-Phase	: Mixer LDPE Materials
Table II	in a Static

	Glass Tı Tempera	ransition tture (°C)					ç				
	A Low- Temperature Block	A High- Temnerature	Molecula	r Weight	Coe Therm Expa	efficient (lal Volum unsion ×	of netric 10	Polydispersity Coefficient	Share of Block	Free Volume	Temperature of the Beginning of Flow
No. ^a	$(T_{g1}^{}/T_{g2}^{})$	Block	$ar{M}_n imes \ 10^{-3}$	$ar{M}_w imes \ 10^{-3}$	α_1	α_2	α_3	K	e	V_f	$T_f(^{\circ}C)$
1	-67		6.16	8.46	9.52	26.0		1.37	0.73	0.102	
		62	209.2	214.5			57.1	1.03	0.27	0.313	102
0		49	218.0	258.3	10.93	41.67		1.2		0.297	96
က		51	262.3	330.5	9.09	38.46		1.3		0.285	100
4		43	128.7	178.8	9.85	37.88		1.4		0.266	97
5		49	289.8	621.3	10.57		36.5	2.15	1.0	0.258	96
9		43	261.6	510.1	11.69		40.4	1.95	1.0	0.273	96
7	-62/25		2.98/2.03	4.70/2.65	5.76	22.9		1.39/1.32	0.31/0.41	0.109	
		36	463.4	547.0			36.1	1.18	0.28	0.115	95
00	-105/-3		0.83/2.02	1.20/2.47	9.52	20.1		1.45/1.22	0.56/0.29	0.053	
		43	470.0	628.0			64.1	1.34	0.19	0.417	98
6		42	397.0	368.3	9.62	44.78		1.1		0.332	95
10		35	654.3	716.6	9.30	38.70		1.1		0.272	97
11	-52		5.23	7.48	9.37	23.81		1.43	0.68	0.096	
		29	297.0	930.0			23.8	3.13	1.0	0.126	98
12		38	520.2	884.5	12.57		37.7	1.70	1.0	0.235	100
13		46	337.8	493.3	11.36		45.5	1.46	1.0	0.327	100
14	-38		13.66	18.68	10.35	37.6		1.37	0.78	0.192	
		41	45.3	254.8			37.6	5.6	0.22	0.257	96
15	-87		4.76	6.26	7.13	31.20		1.3	0.87	0.134	
		43	344.0	688.4				2.0	0.13	0.228	93
16		47	170.5	271.2	12.92	42.60		1.6		0.285	95
a N	o. of composition a	ccording to Table]									

No.ª	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$	$ar{M}_n~ imes~10^{~-~3}$	$ar{M}_w~ imes~10^{~-~3}$	K	$lpha_1 imes 10^{-5}$	$lpha_2 imes 10^{-5}$	V_{f}	T_f (°C)
17	31	323.5	1211.0	3.8	11.02	33.7	0.209	98
18	39	474.4	614.8	1.3	10.70	34.6	0.224	97
19	41	712.9	975.4	1.4	13.50	46.60	0.312	101
20	43	693.8	832.5	1.2	11.36	43.00	0.300	103

Table IIITemperatures of Structural-Phase Transitions and Molecular Parameters of LDPEMaterials Modified in a Dynamic Mixer

^a No. of composition according to Table I; abbreviations, see Table II.

duction of M_n and increased concentration of macromolecular branching fragments (K = 5.6).

Based on the results obtained, a conclusion can be derived that variations of shear intensity in the melt at IA grafting effects not only LDPE-g-IA yield, but the molecular structure of the formed product and its relaxation behavior as well.

LDPE Modified in the Dynamic Mixer

All compositions obtained in the dynamic mixer show the single block structure with one relaxation transition above a room temperature (Table III).

The temperature of transition from glassy to the high-elastic state T_g depends little on the composition content. At DCP introduction the structure compaction reduces, results of a free volume. The molecular weight of polyethylene (Fig. 4) varies similarly to V_f parameters. It increases with DCP concentration almost twofold. Simultaneously, polydispersion was reduced. Just by these parameters the properties of LDPE blended with IA and LDPE-g-IA produced in the dynamic mixer differ in principle from those of compositions obtained in the static mixer. As it is seen from Figure 4 in the latter case, the dependence of \overline{M}_n on an initiator content is of extreme character. Besides, the DCP concentration at which the maximum of \bar{M}_n values are reached is conditioned by the mixer shearing rate also. This fact confirms the role of mechanical action at the formation of the LDPE-g-IA molecular structure.

Let us analyze the effect of mixing conditions (type of mixer and a shearing rate) at the initiator concentration corresponding to the maximum shape of the MWD of LDPE materials (Fig. 4). When a static mixer with a shearing rate of 50 s⁻¹ is used in the presence of 0.2 wt % of DCP, the curve looks like the MWD with undivided bimodality [Fig. 5, curve (3) composition (7)] and a practically equal weight fraction ratio. If the

mixer with a shearing rate of 100 s^{-1} is used, the MWD displays the character analogous to LDPEg-IA upon low-velocity mixing [Fig. 5, curve (1) composition (12)] but has a wider distribution. The production of compositions in the dynamic mixer intensifies the process of polymer division into fractions. Bimodality in compositions 7 and 12 was only slightly displayed when the divided bimodality is found in the composition (19) [Fig. 5, curve (2) composition (19)].

The mechanism of reactions in the given mixing conditions can be described by approximately being based only on the data obtained above. Particularly, it could by supposed with the account of the received data and those from other works¹⁵, where the reason for the MWD bimodality for LDPE-g-IA obtained in dynamic mixing is raised



Figure 4 The dependence of molecular weight of LDPE-g-IA chain fragments in a high-temperature block vs. DCP concentration in compositions (17)–(20) curve (1), compositions (5)–(8) curve (2), and compositions (11)–(14) curve (3); in brackets, numbers of compositions (17), (12), and (19) are given, where MWD are given in Figure 5



Figure 5 The MWD of LDPE-*g*-IA in composition (12) curve (1), composition (19) curve (2), and composition (7) curve (3).

to the homogenization degree of the reactive blend and the higher grafted product yield compared with static mixers.

The resulting data agree well with those from the other works¹⁵ in the conclusion that the mixer type substantially affects the structure of the LDPE-g-IA amorphous phase.

Effect of IA Introduction

The effect of the LDPE interaction with IA in the presence and without DCP in different mixing regimes has been analyzed randomly on samples (2)–(4) (interactions at a shearing rate below 30 s⁻¹); on samples (9) and (10)—DCP-initiated grafting in a static mixer with a shearing rate of 50 s⁻¹; (15) and (16)—the process initiated in a static mixer at a shearing rate of 100 s⁻¹. The results of such analysis are given in Table II. All these compositions except for number (15) are uniblock, with one relaxation transition at 35–51°C, have the temperature of a polymer flow of 90–100°C and almost independent of compactness and polymer chain rigidity. Parameter V_f varies between 0.266 and 0.332.

A diblock structure with two relaxation transitions at -87 and 43° C temperatures is formed in the polyethylene with 2 wt % of IA and 0.3 wt % of DCP. Concentration of a low-temperature block in such a composition is the maximum out of all other studied compositions ($\varphi = 0.87$).

In Figure 6, the dependencies of molecular weight \overline{M}_n on IA concentration in three series of compositions are shown. The effect of a shearing rate applied in the static mixer on the composition molecular-chemical transformations is clear. Low shearing of the mixing of compositions (9)and (10) leads, as it is seen from the figure, to a continuous growth of molecular weight with increasing acid concentration. Due to this fact, it can be stated that the reactions of chain growth decelerate branching and chain degradation processes in these conditions. A low coefficient of polydispersity *K* supports the above supposition. An increase in a shearing rate up to 100 s^{-1} in the mixer changes the shape of \overline{M}_n , depending on the IA concentration. It becomes extreme and proves that there are several competing reactions of growth and chain break [Fig. 6, curve (2)]. The reaction of chain branching is no doubt also running. Absolute values of the polydispersity coefficient K reducing with increased acid content also make possible a similar conclusion. All these fac-



Figure 6 The dependence of the LDPE molecular weight on IA concentration in compositions (9) and (10) curve (1), compositions (15) and (16) curve (2), and compositions (2)-(4) curve (3).



Figure 7 The MWD of LDPE in composition (3) curve (1), composition (15) curve (2), and composition (9) curve (3).

tors influenced the MWD shape shown in Figure 7. Absence of the branching reaction in composition (9) helps, as seen in Figure 7, unimodal and symmetric MWD. The divided bimodality of MWD in compositions (3) and (15) is a result of mechanical and chemical transformations.

CONCLUSIONS

Thermomechanical spectroscopy helps to record noticeable variations in a structure of polyethylene even at slight differences in the efficiency of the monomer grafting or polymer melt viscosity. Thus, for example, for LDPE-g-IA compositions (8), (14), and (20) (Table I) with 1 wt % of IA and 0.3 wt % of DCP, the efficiency of the grafting varies within about a 10% range, MFI varies from 2.5-4.3 g/10 min, and they show very different temperatures of relaxation transitions, molecular weight values, types of thermomechanical curves, and other parameters of the LDPE molecular structure. The data obtained reflect chemical transformations of LDPE molecules in IA's presence without an initiator of the radical reactions (DCP). Most probable is the IA initiation of molecular crosslinking reactions. Also, IA thermodegradation and oligomerization could occur. LDPE and IA or products of acid chemical transformations do not agree thermodynamically [the calculated solubility parameters are 16.1 (MJ/

 m^{3})^{0.5} for polyethylene and 26.4 (MJ/m³)^{0.5} for IA]. From the above procedure it can be supposed that nongrafted IA (or its oligomers) exerts an antiplastifying effect on LDPE and LDPE-g-IA. This assumption should be also taken into consideration when processing experimental data presented in Tables II and III.

The reason for the MWD bimodality for LDPEg-IA obtained in dynamic mixing is the raised homogenization degree of the reactive blend and the higher grafted product yield compared with static mixers. The mixer type substantially affefcts the structure of LDPE-g-IA amorphous phase.

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