Korean J. Chem. Eng., **28**(10), 2057-2063 (2011)
DOI: 10.1007/s11814-011-0080-y

Dynamic-mechanical behavior of polyethylenes and ethene-/α-olefin-copolymers: Part III. γ-relaxation

Florian J. Stadler*,**,†

*School of Semiconductor and Chemical Engineering, Chonbuk National University,
Baekjero 567, Deokjin-gu, Jeonju, Jeonbuk 561-756, Korea
**Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nürnberg,
Martensstr. 7, D-91058 Erlangen, Germany
(*Received 22 November 2010 • accepted 24 March 2011*)

Abstract−The temperature- and frequency-dependent dynamic-mechanical properties in the temperature regime of the γ-transition were determined for a number of polyethylenes and ethylene/α-olefin-copolymers differing in their crystallinity and crystal morphology. The temperature dependence of the γ-transition was found to obey the Arrhenius law for thermally activated processes. The γ-transition temperature determined at a frequency of 1 Hz and the corresponding activation energy were analyzed as a function of the crystallinity. As an overall trend, both quantities are found to decrease with decreasing crystallinity, which is explained by the increase in free volume due to the incorporation of short-chain branches or the thermal pretreatment (e.g., quenching). Taking into account that the crystal morphology of polyethylenes can be classified into four different groups, a more detailed picture appears. Within one type of morphology both quantities, namely the transition temperature and the activation energy, increase with decreasing crystallinity independent of the α-olefin used as the comonomer. These findings can be explained by partial orientations of the molecule segments in the interlamellar amorphous space in the case of HDPE or by the increased steric hindrance of the crankshaft motion by the short-chain branches. From the findings of this series of studies, it was concluded that the glass transition in polyethylene and polyethylene/α-olefin-copolymers is the β- and not the γ-transition.

Key words: γ-Relaxation, Polyethylene, Ethylene/α-olefin-copolymer, Dynamic-mechanical Properties, Activation Energy

INTRODUCTION

Dynamic-mechanical properties are often used to understand solid state properties in terms of identifying the different molecular relaxation processes of a polymer. Among the materials studied, polyethylene and its copolymers with α-olefins have received considerable attention, because of the complexity and diversity of their relaxation processes and their high industrial relevance. In polyethylenes and ethylene/α-olefin-copolymers, it is common to label the relaxation processes which occur with decreasing transition temperature as the α-, β- and γ-transitions [1]. In the following, only the experimental results concerning the γ-relaxation in polyethylenes obtained from dynamic-mechanical meas- urements are summarized.

The γ-relaxation in polyethylene homopolymers (linear and branched) was reported to occur at temperatures of around −120 °C. This relaxation was accompanied by a decrease in storage modulus of approximately 30% [2]. Illers [3,4] reported two γ-relaxations from torsional pendulum measurements at a frequency of 1 Hz, one at about −120 °C, which is typical of linear polyethylenes [3], and one at about −140 °C (1 Hz), which is typical of branched polyethylenes [4]. The latter was only found in slowly cooled and tempered samples and often overlapped with the high temperature transition [4]. Khanna et al. [5] reported higher γ-relaxation temperatures at 1 Hz of HDPE (−107 °C) compared to LDPE (−114 °C), which were independent of the thermal prehistory of the samples. They also described an increase in the strength of the γ-relaxation characterized as the maximum in the loss modulus E″ with decreasing crystallinity similar to Illers's findings [3,4]. The work of Matthews et al. [6] revealed an influence of the thermal prehistory on the γ-relaxation temperature for HDPE. For the slowly cooled sample of higher crystallinity, somewhat higher relaxation temperatures (≈−110 °C) were measured compared to the quenched samples, which relaxed at around −120 °C.

The temperature dependence of the transition in polyethylene homopolymers was described by the Arrhenius equation having an activation energy of about 60 kJ/mol for HDPE (high temperature process) [3] and of about 29 kJ/mol for branched LDPE (low temperature process) [4]. An activation energy of 38 kJ/mol was reported by Hartwig [2], whereas Stehling and Mandelkern [1] cited values ranging from 25 to 75 kJ/mol depending on the crystallinity.

Clas et al. [7] showed that for copolymers of ethylene with butene, octene, and octadecene the transition temperature varied only slightly with the type of comonomer used. The activation energy was constant within the experimental accuracy with values of about 90 kJ/mol±20 kJ/mol.

The resumption of the research dealing with the γ-transition started in the late nineties of the last millennium when new polyolefin products, especially LLDPE, became available by synthetic routes using metallocene catalysts. Jordens et al. [8] re-examined the influence of the thermal prehistory on the intensity of the γ-relaxation in tanδ for a linear metallocene HDPE. Their findings were similar to Illers's [3,4] results, in that the intensity increases with decreasing crystallinity. Measurements on metallocene LLDPE with different hexane

---

†To whom correspondence should be addressed.
E-mail: fjstadler@jbnu.ac.kr

contents by Cerrada et al. [9] and by Nitta and Tanaka [10] revealed a decrease of the relaxation temperature and a decrease of the activation energy with decreasing crystallinity viz. increasing comonomer content. Cerrada et al. [9] also reported approximately 5 °C lower transition temperatures for their slowly cooled sampled compared to the quenched ones. Shan et al. [11] also examined ethylene/1-hexene copolymers with different comonomer distributions and found that the transition temperature at 1 Hz at −120 °C was independent of the hexane content, comonomer distribution and thermal prehistory. Benavente et al. [12] reported similar tendencies in both quantities for metallocene catalyzed LLDPE materials with octadecene as comonomer.

From the decrease in the relaxation strength with increasing crystallinity, Boyd and Ward [13,14] concluded that the γ-relaxation is located in the amorphous regime.

The molecular mechanism behind the γ-relaxation is frequently reported as the so-called crankshaft motion. In this motion (Fig. 1), neighboring CH_2-groups (three to five monomer units [15,16]) rotate around their common bond axis to relax mechanical stresses (Hartwig [2], Boyd [17]).

In conclusion, it can be stated that significantly different values have been reported with respect to the temperature of the γ-transition and its activation energy.

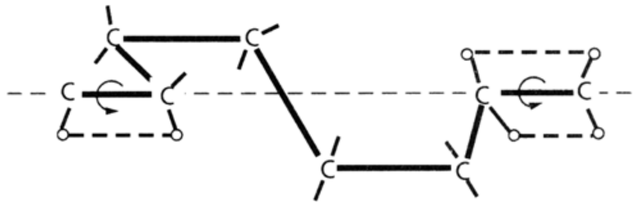

Fig. 1. Crankshaft motion (republished with kind permission of Hartwig [2]).

This paper aims to broaden the experimental data base in the γ-relaxation regime by carefully performed dynamic-mechanical measurements over a broad range of frequencies. By evaluating the data measured for a number of commercially available polyethylenes (HDPE, LDPE) and ethene/α-olefin copolymers (LLDPE), a clarification of the influence of the chemical structure and, thus, of the crystallinity and morphology on the temperature of the γ-relaxation as well as on its activation energy is attempted. Besides the effect of the chemical structure, the influence of the thermal preconditioning on the crystallinity and morphology and, consequently, on the γ-relaxation is investigated. Also an answer to the question of the nature of the γ-transition will be searched for. As this is closely connected with the nature of the β-transition, a discussion, on which of these relaxations is the glass transition, will conclude this paper.

EXPERIMENTAL

The α- and β-relaxations were investigated for a number of commercially available polyethylene grades and have been presented elsewhere [18,19]. For these materials the results in the γ-transition regime are presented herein. Their physical characteristics are summarized in Table 2. The experimental details as well as some molecular characteristics are described in part I [18] of this series of articles.

RESULTS AND DISCUSSION

The γ-relaxation was observed for all of the samples under investigation. It can be identified either from the loss modulus or from the loss factor tanδ. As is well known, the maximum of the loss modulus occurs at lower temperatures compared to the maximum of the tanδ. As the measuring temperature is limited to −145 °C, tanδ was chosen to analyze the γ-relaxation temperature in order to

Table 1. Melting temperatures, densities, and crystallinity for the materials investigated

Name	Quenched samples			Slowly-cooled samples		
	Melting temperature T_m [°C]	Density [g/cm³]	Crystallinity x_v [%]	Melting temperature T_m [°C]	Density [g/cm³]	Crystallinity x_v [%]
HDPE 1	139.6	0.947	70	139.4	0.970	80
HDPE 2	133.2	0.937	61	133.6	0.948	68
HDPE 3	135.0	0.940	63	135.1	0.949	68
HDPE 4	133.9	0.933	58			
LLDPE 1	124.1	0.919	48			
LLDPE 2	115.3/123.0[a]	0.915	45			
LDPE 1	110.4	0.915	45	110.4	0.919	48
LLDPE 3	115.8	0.913	44			
LLDPE 4	112.2	0.910	42			
LLDPE 5	106.7	0.904	37			
LLDPE 6	101.4	0.898	33			
LLDPE 7	100.4	0.898	33	100.9	0.901	35
LLDPE 8	97.8	0.897	32	96.9	0.902	36
LLDPE 9	94.0	0.896	32			
LLDPE 10	97.1	0.893	30			
LLDPE 11	44.1/63.5[a]	0.871	13			

[a] Two discrete melting temperatures were observed

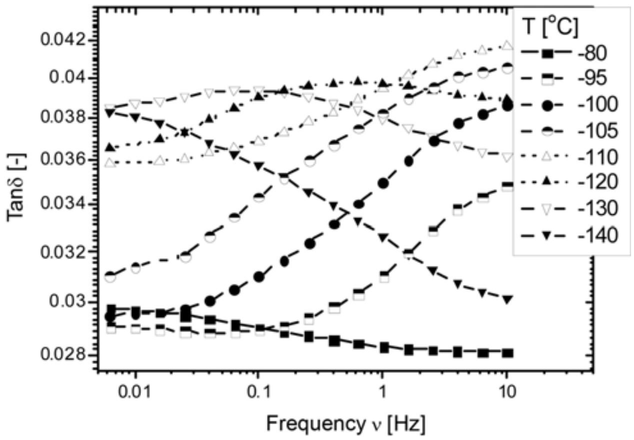

Fig. 2. tanδ as a function of frequency for quenched LLDPE 8 at different temperatures in the γ-transition regime.

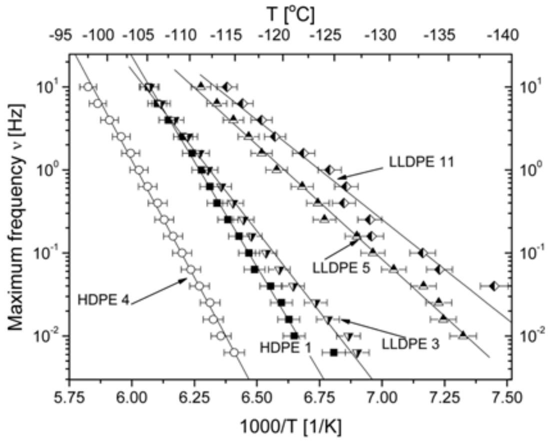

Fig. 4. Arrhenius-plots of γ-relaxation frequencies of six different polyethylenes.

have as wide as possible a temperature window, in which this relaxation occurs.

The plot of the loss factor tanδ as a function of the frequency, ν, at different temperatures, T, (Fig. 2) reveals a damping maximum attributed to the γ-relaxation in the temperature range displayed. An increase in temperature results in a shift of the experimental curve to higher frequencies.

It is also clear from Fig. 2 that the material is thermorheologically complex, i.e., that a shift along the frequency axis cannot be used for creating a master curve [20,21]. Considering that any crystalline material has at least two phases (amorphous and crystalline), this is not surprising, because these different phase have different temperature dependencies, which were studied in detail for block-copolymers [22-26]. Block-copolymers are a good material to use for comparison, as both semi-crystalline polymers and block-copolymers have two (or more) phases, differing in their physical behavior but which are, nevertheless, chemically attached to each other.

The frequency sweeps were converted into the temperature dependencies at a fixed frequency (cf. Fig. 3). In this plot, the determination of the temperature of the damping maximum tanδ(T) is quite possible. By using the tanδ-maxima at each frequency, the determination of the activation energy can be achieved via the Arrhenius plot (see Fig. 4).

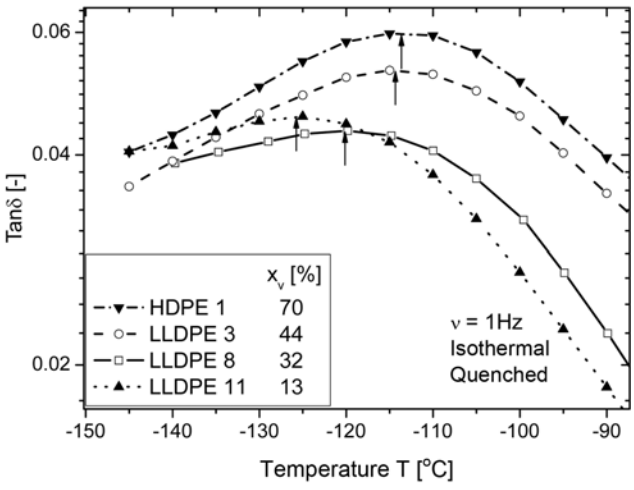

Fig. 3. γ-Relaxation as measured in the temperature dependence of tanδ at a frequency of 1 Hz of four different polyethylenes, where the arrows (↑) indicate the temperature of the maximum, T_γ(1 Hz).

Fig. 3 shows the γ-transitions of four different samples with crystallinity x_v between 13 and 70%. For the quenched HDPE 1 with a crystallinity of 70%, a maximum in the tanδ of 0.06 is found, while the quenched LLDPE 11 with a crystallinity of 13% has a maximum intensity of tanδ=0.045 only. The asymmetry of the damping peak is probably due to an additional relaxation observed at temperatures slightly below the γ-relaxation, which is attributed to a mechanism whose origin is somewhat unclear but is assumed to be similar to that of the γ-relaxation [1,2,27,28].

The dependence of the relaxation intensity on the crystallinity is in contradiction to the literature. The intensity of the γ-relaxation expressed by the maximum tanδ increases with increasing crystallinity (Fig. 3). However, Khanna et al. [5] reported the opposite effect. An explanation of this will be given later. The γ-transition temperature T_γ (1 Hz), determined from the maxima in Fig. 3, decreases, as a general trend, with decreasing crystallinity, which is in agreement with the literature [1-14].

As the measurements were performed in the form of isothermal frequency sweeps, the relaxation temperatures are determined for each single frequency as shown in Fig. 3 for a frequency of 1 Hz. Plotting the measuring frequency in the Arrhenius diagram as a function of the reciprocal of the corresponding temperature of the maximum in tanδ allows for the detailed analysis of the temperature dependence of the γ-relaxation. Fig. 4 gives this plot for six representative samples. The error in the determination of the temperature of the maximum is estimated to be ±1 K. If the maxima in tanδ as a function of temperature are very broad and overlap with the additional process, the analysis is difficult. This happens only at the lowest frequencies at temperatures below −135 °C (see Fig. 3), which leads to the larger scattering of the data for LLDPE 5&11 at low frequencies (Fig. 4).

Fig. 4 shows clearly that all of the materials follow the Arrhenius equation (linear relation in logν(1000/T)) with a sample dependent activation energy E_a. Table 2 compiles the characteristic data of the

Table 2. Temperatures T_γ(1 Hz) and activation energies $E_a(\gamma)$

Name	Morphology type	Quenched samples			Slowly-cooled samples		
		Crystallinity x_v [%]	E_a (γ) [kJ/mol]	T_γ (1 Hz) [°C]	Crystallinity x_v [%]	E_a (γ) [kJ/mol]	T_γ (1 Hz) [°C]
HDPE 1	IV	70	97	−114	80	95	−106
HDPE 2	IV	61	110	−109	68	118	−116
HDPE 3	IV	63	99	−113	68	110	−112
HDPE 4	IV	58	108	−107			
LLDPE 1	III	48	95	−111			
LLDPE 2	III	45	72	−117			
LDPE 1	III	45	49	−118	48	43	−123
LLDPE 3	III	44	74	−114			
LLDPE 4	III	42	106	−113			
LLDPE 5	II	37	53	−121			
LLDPE 6	II	33	68	−114			
LLDPE 7	II	33	48	−119	35	64	−114
LLDPE 8	II	32	46	−121	36	48	−121
LLDPE 9	II	32	82	−114			
LLDPE 10	II	30	62	−119			
LLDPE 11	I	13	46	−126			

γ-relaxations of the different samples.

In this table the morphology classification published by Bensason et al. [29] is added and allows interesting conclusions to be drawn for the ethylene homopolymers and ethene-/α-olefin-copolymers. Bensason et al. [29] described four different crystalline morphologies observed in polyethylene and ethylene/α-olefin-copolymers:

- Type IV: Highly ordered, i.e., crystallinity x>55%, highly lamellar crystallites, found in HDPE.
- Type III: Medium order, 40<x<55%, lamellar crystallites, found in LLDPE.
- Type II: Low crystallinity, 30<x<40%, mixture of bundle and lamellar crystallites, found in plastomers.
- Type I: very low crystallinity, x>30%, bundle crystallites, found in elastomers.

The quenched HDPEs (type IV-morphology) show activation energies E_a of the γ-relaxation between 95 and 120 kJ/mol and relaxation temperatures at 1 Hz of around −110 °C. For LLDPEs with a type III-morphology, the values are 80 kJ/mol and −115 °C, respectively. The LLDPEs with a higher comonomer content (e.g., plastomers and elastomer grades) are of type II/I-morphology and have the lowest activation energies of the γ-relaxation of around 50 kJ/mol and the lowest relaxation temperatures of around −120 °C. The influence of the cooling conditions (measured for LLDPE 7, LLDPE 8, and LDPE 1) was found to be small. For the short-chain branched samples, the cooling conditions have little effect on either the crystallinity or the crystal structure.

Table 2 clearly demonstrates that the characteristic parameters of the γ-relaxation are dependent on the morphology of the polyethylene. Therefore, the results obtained are analyzed in more detail for linear and short-chain branched samples having different crystal morphologies.

1. HDPE (Morphology Type IV)

Fig. 5 gives the dependence of the γ-relaxation temperature measured at 1 Hz, T_γ (1 Hz), on the crystallinity of the HDPE samples. With the exception of the slowly cooled HDPE 1 and HDPE 3 a linear decrease of T_γ (1 Hz) with increasing crystallinity can be assumed with a slope of −0.8 °C per percent increase in crystallinity. The data of Jordens et al. [8] indicate a similar trend. Only the highly crystalline samples of the slowly cooled HDPE 1 and HDPE 3 deviate significantly from this dependence. This finding is surprising, as the opposite trend would be expected from the literature.

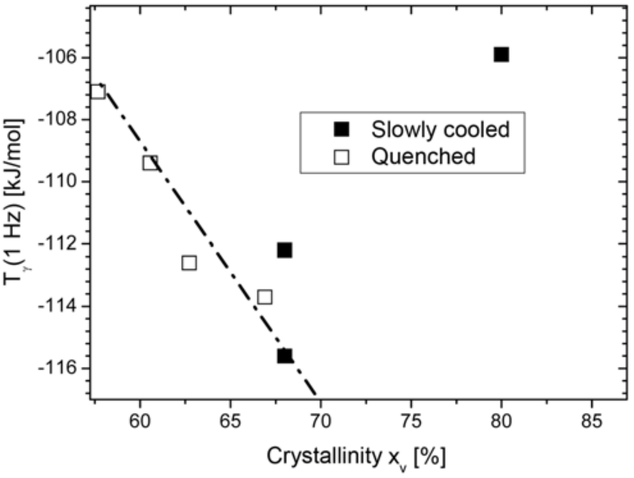

Fig. 5. Dependence of the γ-transition temperature T_γ (1 Hz) on the crystallinity for the HDPE-samples (line drawn as a guide for the eye).

A similar picture is revealed by Fig. 6, where the activation energy $E_a(\gamma)$ is plotted as a function of the crystallinity. In this picture the results for the two sample conditions, slowly cooled and quenched, are clearly separated. Again a decrease of the activation energy with increasing crystallinity can be identified for both sample preconditions. The linear dependence with a slope of −0.9 kJ/mol per percent crystallinity is assumed to be valid for the quenched samples

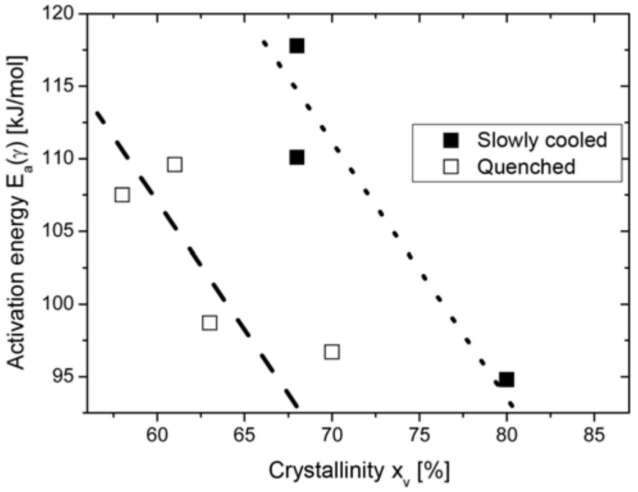

Fig. 6. Dependence of the activation energy of the γ-transition $E_a(\gamma)$ of the HDPE on the crystallinity (the lines are drawn as a guide for the eye).

within the experimental accuracy. The slowly cooled materials exhibit the same slope, but have a higher activation energy (about 20 kJ/mol) at comparable crystallinity.

To explain the findings, the following assumptions are made:

As proposed in the literature [2,15-17], it is assumed that the γ-relaxation takes place due to the crankshaft motion in the amorphous regime and/or in the interfacial region close to the crystal lamella surfaces. Furthermore, the γ-relaxation will occur only if the molecular mobility generated by the thermal energy is high enough and if sufficient intermolecular space (free volume) is accessible for the rotation of the molecule segments. The crucial assumption is that the energy barrier for the rotation will decrease, if the rotating moieties are oriented parallel to the rotation axis. As the crankshaft motion involves only a few carbon atoms (about 6 to 10), it is reasonable to suppose that the oriented parts of the chains undergo the movement more easily, as less intermolecular space, i.e., free volume, is necessary. The latter is equivalent to a lower energy barrier for the motion, which has to be overcome by thermal activation.

In this context, the decrease of both the relaxation temperature T_γ (1 Hz) and the activation energy $E_a(\gamma)$ with increasing crystallinity can be explained as follows. As the crystallinity is quite high, the interlamellar distances, which determine the width of the amorphous regime between the crystal lamellae, are thin for HDPE. The interlamellar spacing is found to be constant for polyethylenes of sufficiently high molar mass (M_w>=100 kg) [30,31]. For such materials, it was shown also that the spacing has a value of about 9 nm and does not depend on the crystallinity in the range between 20% and 70% [25]. This distance is equivalent to the end-to-end distance of an extended chain of 35 monomer units and, thus, is much larger than that of the 3 to 5 monomer units involved in the crankshaft motion. Partial orientations in the interlamellar space are generated during the crystallization process as tensile stresses generated due to the volume shrinkage may orientate the short polymer segments in the amorphous regimes. As the interlamellar spacing is quite small, the oriented segments are not able to relax. If the crystallinity increases, the volume shrinkage and, thus, the internal stress on the molecules increases leading to a higher number of oriented segments or to higher degrees of orientations in the individual segments. Consequently, the energy barrier for the crank-shaft motion inevitably decreases and this is reflected in the lower activation energy and lower transition temperature. Therefore, both quantities T_γ (1 Hz) and $E_a(\gamma)$ will decrease with increasing crystallinity.

With this picture in mind, an explanation of the influence of the sample pretreatment is also possible. The slowly cooled samples have the same activation energy, but higher crystallinity. This implies that the thermal pretreatment only influences the crystalline regions but not the local orientation of parts of the chains in the amorphous regimes.

An explanation for the deviation in the relaxation temperature (see Fig. 5) of the material with the highest crystallinity (80%, HDPE 1 slowly cooled) is provided by this model, too. The crystallinity of the slowly cooled HDPE 1 is above the threshold of 70%, and a much smaller interlamellar spacing of about 4.8 nm was found [8]. Tanem and Stori [32] reported a thickness of the amorphous layer of only 3.4 nm for a polyethylene, which is comparable to the HDPE 1. Jordens et al. [8] also reported similar values. If the dimensions of the amorphous region come to have the same order of magnitude as those of the moving chain entities, additional free volume has to be generated by thermal expansion in order to allow the motion to occur. This is reflected by the higher value of the transition temperature in the highly crystalline HDPE.

2. LLDPE and LDPE (Morphology Types I/II, III)

When analyzing the dependence of T_γ (1 Hz) (Fig. 7) and $E_a(\gamma)$ (Fig. 8) on crystallinity for LLDPE and LDPE, a more complicated picture appears. As general trend, an increase of both quantities with increasing crystallinity is observed. This trend is shown by the dashed arrows in Fig. 7 and Fig. 8. The insertion of comonomer into the polyethylene lowers the crystallinity because of the disturbance of the regularity of the molecular architecture. The free volume is also increased due to the additional end groups of the short-chain branches in the amorphous region. This increase in the free volume was confirmed by the analysis of the amorphous scatter background in X-ray measurements of ethene/α-olefin copolymers having different comonomer contents [30,31]. A larger intermolecular spacing, in general, decreases the energy barrier for the move-

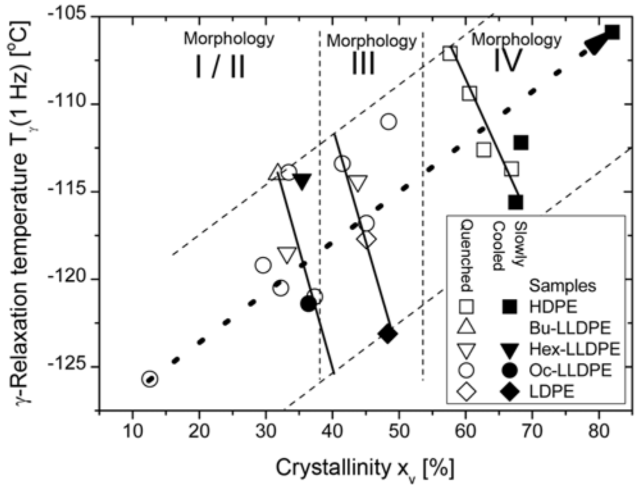

Fig. 7. Dependence of the γ-transition temperature on the crystallinity for all of the samples investigated.

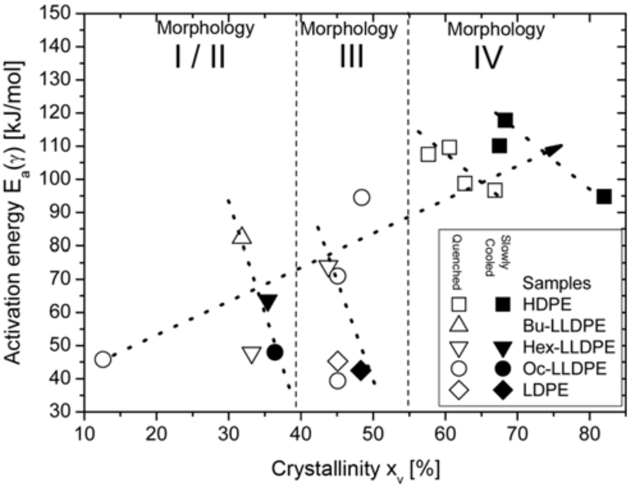

Fig. 8. Dependence of the activation energy of the *γ*-transition on the crystallinity for all of the samples investigated.

ments of the molecular segments and, thus, the relaxation temperature.

In Figs. 7 and 8, the regimes of different morphology types are indicated by the dashed lines. The dependencies within one morphology class are similar to those already discussed for HDPE (morphology type IV), namely, an increase of the relaxation temperature and activation energy with decreasing crystallinity. A change in morphology, e.g., from type IV to III or from type III to II/I, results in a decrease of the relaxation temperature of about 10 K and a decrease of the activation energy of about 50 kJ/mol.

In the case of the short-chain branched LLDPES and the LDPE, not only the additional free volume stemming from the end groups of the branches have to be taken into account but also the influence of the short-chain branches on the crank-shaft motion. It is reasonable to suppose that the short chain branches will act as a steric obstruction to the crankshaft motion. This hindrance results in a higher energy barrier to be overcome and, thus, higher relaxation temperatures.

CONCLUSIONS

1. *γ*-Relaxation

The temperature of the *γ*-relaxation, T_γ (1 Hz), and its activation energy, $E_a(\gamma)$, were determined for a number of polyethylenes and ethene/*α*-olefin copolymers from dynamic-mechanical measurements covering a frequency range of more than three orders of magnitude. Both quantities depend on the crystallinity.

As overall trend, increases of T_γ (1 Hz) and $E_a(\gamma)$ with increasing crystallinity were found, which is in agreement with previous reports [1-7,9-14,33]. The span of the activation energies and relaxation temperatures is in agreement with the sparse data published in the literature [34]. The overall trend could be explained by the additional free volume resulting from the end groups in the amorphous region, which lowers the activation energy and, therefore, the relaxation temperature.

Within one morphology, the opposite dependence was found. The increase of the relaxation temperature and activation energy could be explained by the segment orientation in the amorphous regime caused by the crystallization process in the highly crystalline HDPE's of morphology type IV. For LDPEs and LLDPEs the steric hindrance of the short-chain branches accounts for the increase in the activation energy and relaxation temperature.

These findings suggest that within one morphology the influence of the sterical obstruction stemming from the side chains is stronger than that resulting from the increase in the free volume. When polyethylene changes to a less ordered morphology, its free volume is drastically increased, which leads to a decrease in T_γ of about 10 K and in $E_a(\gamma)$ of about 50 kJ/mol.

2. Glass Transition of PE

Having analyzed all of the relaxation phenomena in the polyethylenes occurring above – 150 °C (the *α*′-relaxation [18], *α*- and *β*-relaxation [19], and *γ*-relaxation in this work), a final survey of the nature of the *β*- and *γ*-relaxations should be made. Based on the results discussed above and in [19], as well as in the references mentioned therein, it can be concluded that the *β*-transition and *γ*-relaxation correspond to the glass-transition temperature and a segmental, secondary relaxation process in the amorphous regime of the polyethylenes, respectively. This hypothesis is supported by the following facts:

1. The magnitude of the variation of the storage modulus with temperature is only a factor of 2 in the *γ*-transition region, while in the *β*-regime it may exceed one order of magnitude, depending on the crystallinity. The linear dependence of the modulus at temperatures above the *β*-transition allows for the extrapolation to zero crystallinity, from which the entanglement molar mass of polyethylenes was determined [18].
2. As the glass transition typically involves motions on larger length scales, high activation energies (200-500 kJ/mol) are obtained. The activation energies of the *γ*-relaxation were 120 kJ/mol and lower, while for the *β*-transition values between 200 and 450 kJ/mol were determined for the polyethylenes under investigation.

The fact that the *β*-relaxation is not found in HDPE resins is only a contradiction at a first glance. As pointed out in ref. [19] and in this work, the spacing between the lamellae in highly crystalline HDPE attains values ranging from 4 nm for a highly crystalline HDPE up to 9 nm [8,10,30-32,35]. The interlamellar spacing is equivalent to an extended chain length of about 30-70 monomer units corresponding to the molar mass of less than one entanglement. Matthews et al. [6], as well as Stadler [19], argued that the *β*-transition occurs together with the (much stronger) *α*-relaxation in HDPE, because this relaxation softens the lamellae in such a way that the *β*-relaxation can take place.

These arguments all point towards the *β*-relaxation as the glass transition although the *γ*-transition significantly contributes to the chain mobility on a small scale.

ACKNOWLEDGEMENTS

This work was financially supported by the "Human Resource Development (project name: Advanced track for Si-based solar cell materials and devices, project number: 201040100660)" of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy. Discussions with Prof. Dr. Helmut Münstedt and Dr. J. Kaschta, Friedrich-Alexander University Erlangen-Nürnberg greatly contributed to the understanding presented in this work. Additionally, the contributions of Mrs. I. Herzer and Dr. J. Kaschta (Erlangen) regarding the SEC-MALLS measurements and the help of M. Sturm (Erlangen) for the FT-IR measurements are also greatly appreciated.

REFERENCES

1. F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**(2), 242 (1970).
2. G. Hartwig, *Polymer properties at room and cryogenic temperatures*, New York, Plenum Press (1994).
3. K. Illers, *Coll. Polym. Sci.*, **251**, 394 (1973).
4. K. Illers, *Coll. Polym. Sci.*, **252**, 1 (1974).
5. Y. Khanna, E. Turi, T. Taylor, V. Vickroy and R. Abbott, *Macromolecules*, **18**, 1302 (1985).
6. R. G. Matthews, A. P. Unwin, I. M. Ward and G. Capaccio, *Journal of Macromolecular Science-Physics*, **B38**, 1-2, 123 (1999).
7. S. D. Clas, D. C. Mcfaddin and K. E. Russell, *J. Polym. Sci. Part B-Polym. Phys.*, **25**, 5, 1057 (1987).
8. K. Jordens, G. L. Wilkes, J. Janzen, D. C. Rohlfing and M. B. Welch, *Polymer*, **41**, 19, 7175 (2000).
9. M. L. Cerrada, R. Benavente, B. Pena and E. Perez, *Polymer*, **41**, 15, 5957 (2000).
10. K. H. Nitta and A. Tanaka, *Polymer*, **42**, 1219 (2001).
11. C. L. P. Shan, J. B. P. Soares and A. Penlidis, *Polymer*, **43**, 3, 767 (2002).
12. R. Benavente, E. Perez, M. Yazdani-Pedram and R. Quijada, *Polymer*, **43**, 25, 6821 (2002).
13. R. H. Boyd, *Polymer*, **26**, 323 (1985).
14. I. M. Ward and D. W. Hadley, *The yield behaviour of polymers*, In Sons, J. W., Ed., *Polymer*, Chichester, England, **11**, 213 (1993).
15. R. Boyer, *Rubber Chem. Technol.*, **34**, 1303 (1963).
16. T. Shatzki, *J. Polym. Sci.*, **57**, 496 (1962).
17. R. H. Boyd, *Polymer*, **26**, 1123 (1985).
18. F. J. Stadler, J. Kaschta and H. Münstedt, *Polymer*, **46**(23), 10311 (2005).
19. F. J. Stadler, *Korean J. Chem. Eng.*, **28**(3), 954 (2011).
20. F. J. Stadler, J. Kaschta and H. Münstedt, *Macromolecules*, **41**(4), 1328 (2008).
21. J. A. Resch, F. J. Stadler, J. Kaschta and H. Münstedt, *Macromolecules*, **42**(15), 5676 (2009).
22. F. S. Bates, J. H. Rosedale and G. H. Fredrickson, *J. Chem. Phys.*, **92**(10), 6255 (1990).
23. K. Almdal, F. S. Bates and K. Mortensen, *J. Chem. Phys.*, **96**(12), 9122 (1992).
24. F. J. Stadler, *Express Polym. Lett.*, **5**(4), 327 (2011).
25. U. Gaur and B. Wunderlich, *Macromolecules*, **13**(6), 1618 (1980).
26. L. Leibler, *Macromolecules*, **13**(6), 1602 (1980).
27. E. Laredo, N. Suarez, A. Bello and L. Marquez, *J. Polym. Sci. Part B-Polym. Phys.*, **34**(4), 641 (1996).
28. E. Laredo, N. Suarez, A. Bello, B. R. d. Gascue, M.A. Gomez and J.M.G. Fatou, *Polymer*, **40**, 6405 (1999).
29. S. Bensason, S. Nazarenko, S. Chum, A. Hiltner and E. Baer, *Polymer*, **38**, 14, 3513 (1997).
30. F. J. Stadler, T. Takahashi and K. Yonetake, *e-Polymers*, **40** (2009).
31. F. J. Stadler, T. Takahashi and K. Yonetake, *e-Polymers*, **41** (2009).
32. B. S. Tanem and A. Stori, *Polymer*, **42**, 6609 (2001).
33. S. Głowinkowski, M. Makrocka-Rydzyk, S. Wanke and S. Jurga, *European Polym. J.*, **38**, 5, 961 (2002).
34. Most of the activation energies determined were significantly larger than the value of 38 kJ/mol reported by Głowinkowski et al. [33] and Hartwig [2]. The reason for these differences might lie in the measurement method, as both groups determined the activation energy by NMR, which seems not to produce comparable results with dynamic- mechanical measurements due to the different length scales being analyzed (see also part II of this series [19]).
35. R. Popli, M. Glotin and L. Mandelkern, *J. Polym. Sci. Part B: Polym. Phys.*, 407 (1983).