Dedicated to Dr. Igor Dvornik on his 85 birthday

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Calorimetric investigation of high conversion homopolymerization, graft polymerization and copolymerization reactions

Abstract

The calorimetry was used to follow the course of polymerization, graft polymerization and copolymerization reactions. Comparison with widely used point-by-point methods has been performed. Great advantages of calorimetry are direct and continuous measurement of the reaction rate independently from the physical state of reaction system and using only one sample for the whole conversion range. The accuracy and sensitivity achieved are better than those achieved by other methods.

The gel-effect which is not pronounced in the spontaneous polymerization of styrene and could not be easily detected with other methods has been readily detected by calorimetry. Calorimetric investigation of grafting kinetics of styrene and methylmethacrylate on air-preirradiated polyethylene have shown that in low density polyethylene peroxides have the dominating role in the grafting reaction, while in high density polyethylene peroxy radicals have a significant role. The change of the viscosity of reaction medium in the course of grafting reaction as well as the structure of polymer influence the kinetics of reaction. The decay of active species in time can be followed by calorimetry.

The great advantage of calorimetry was demonstrated in investigation of the copolymerization of electron donor and electron acceptor monomers. It was observed that the alternating copolymerization of α-methylstyrene with maleimides, regardless of ratio of comonomers in the feed, and the homopolymerization of maleimides are not simultaneous but are consecutive reactions. Homopolymerization starts only after the completion of alternating copolymerization when α-methylstyrene is exhausted. The end of copolymerization and start of homopolymerization was strictly detected by calorimetry. The conversion of alternating copolymer was close to theoretically expected. α-Methylstyrene as a strong electron donor forms stable charge transfer complexes with electron acceptors like maleimides. The competitive character of copolymerization and homopolymerization is a consequence of the participation of charge transfer complex in the copolymerization reaction.

KEY WORDS
alternating copolymerization
calorimetry
charge transfer complex
gel-effect
graft polymerization
high conversion polymerization

KLJUČNE RIJEČI:
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kalorimetrija
kompleks s prijenosom naboja
naizmjenična kopolimerizacija
polimerizacija
visoka konverzija

Kalorimetrijsko istraživanje homopolimerizacije, cijepljenja i kopolimerizacije do visokih konverzija

Sažetak

Kalorimetrijom je praćen tijek homopolimerizacije, polimerizacije cijepljenjem i kopolimerizacije. Usporedbom s najčešće korištenim metodama pokazane su velike prednosti kalorimetrije: neposredno i kontinuirano mjerenje brzine reakcije neovisno o fizičkom stanju sustava te upotreba samo jednog ispitka u cijelom području konverzija. Točnošću i osjetljivošću mikrokalorimetrija nadmašuje ostale metode.

Gel-efekt, koji je drugim metodama teško zamijetiti u spontanoj polimerizaciji stirena, lako je zamijećen kalorimetrijom.

Kalorimetrijsko istraživanje kinetike cijepljenja stirena i metil-metakrilata na polietilen prethodno ozračen na zraku pokazalo je da u polietilenu niske gustoće peroksidi imaju glavnu ulogu u reakciji polimerizacije cijepljenjem, dok su u polietilenu visoke gustoće važni peroksidni radikali. Promjena viskoznosti reakcijske sredine tijekom reakcije polimerizacije cijepljenjem, kao i struktura polimera utječu na kinetiku reakcije. Raspad aktivnih čestica s vremenom također se može pratiti kalorimetrijom.

Velika prednost kalorimetrije pokazana je u istraživanju kopolimerizacije monomera davatelja i monomera primatelja elektrona. Opaženo je da naizmjenična kopolimerizacija α-metilstirena s maleimidima, bez obzira na omjer komonomera u smjesi, i homopolimerizacija maleimida nisu istodobne, nego homopolimerizacija maleimida počinje samo kada je naizmjenična kopolimerizacija završila, tj. kada je α-metilstiren potrošen. Završetak kopolimerizacije i početak homopolimerizacije precizno je određen kalorimetrijom. Prinos naizmjeničnoga kopolimera bio je blizak teorijski očekivanom prinosu. Kao jak davatelj elektrona, α-metilstiren stvara s primateljima elektrona kao što su maleimidi stabilne komplekse s

prijenosom naboja. Natjecateljski karakter reakcija kopolimerizacije i homopolimerizacije posljedica je sudjelovanja kompleksa s prijenosom naboja u reakciji kopolimerizacije.

Introduction

The most of the existing and widely used methods for measuring reaction rate of polymerization processes suffer from basic disadvantages including indirect measurement, insufficient accuracy and limited applicability. Their unsuitability is especially pronounced in the investigation of polymerization reactions at high conversion and in heterogeneous media.

The availability of precise data on the reaction rate is an important prerequisite for the understanding of the reaction mechanism. Numerous doubts and uncertainties connected with the mechanism of polymerization processes are the consequence of limited and insufficient accuracy of available methods for measuring the reaction rate. Since polymerization reactions are usually accompanied by a considerable heat effect, calorimetry appears to be a suitable method for investigation of polymerization processes.

Calorimetry has been used by a number of authors to follow the course of polymerization processes. Transition temperature regions were investigated by programmed temperature increase in the greater part of research done in this field. In measurements performed by the DSC technique at a fixed temperature only a rather low degree of sensitivity and kinetic purity was possible.[1,2] We have applied an adapted Calvet microcalorimeter for investigation of homopolymerization, graft polymerization and copolymerization reactions.

High conversion homopolymerization of styrene

The course of spontaneous polymerization of styrene at 90.15°C was followed by calorimetry and by point-by-point methods.[3,4,5] Prior to polymerization standard purification procedure and prepolymerization of styrene were performed.

Microcalorimetry

A sample of styrene in glass ampula sealed off under vacuum was put into an adapted Calvet-type microcalorimeter and the rate of polymerization was measured for 260 hours up to approximately 97% conversion.

The calorimeter functioned with two cylindrical cells (ø 20 × 80 mm with maximal usable volume 15cm³) situated in a thermostated metal block thus assuring constant temperature. Each cell was surrounded by one thermobattery consisting of 496 thermocouples (chromel-constantan) connected in a series. Thermobatteries were connected in opposition. The recorded electromotive force, i.e. voltage signal was thus equal to the difference of the signals from the cell containing the investigated sample (the measuring cell) and the reference cell. The signal generated in each thermobattery was in proportion to the heat effect in the corresponding cell. The heat effect of the measuring cell consisted of 2 components: heat of the measured reaction and parasitic heat effects not caused by studied reaction (mainly fluctuation of the temperature of a metal block). These parasitic effects can be made identical for both cells.

Since the heat effect of the reference cell is produced only by parasitic effects the calorimeter we used was capable of compensating all small temperature fluctuations of the metal block. In this way high sensitivity is obtained in measuring the signal, which is proportional to the heat flow from the measuring cell through the thermocouples to the block. Therefore, the recorded voltage signal is proportional to the rate of reaction going on inside the measuring cell.

The reaction rate can be calculated from this signal in the following way: If H is the heat of polymerization of the monomer (in J/mol) and M is its molecular weight, the relation

$$Q = \frac{H}{M} \qquad (1)$$

yields the heat Q developed in the case of complete polymerization of one gram of this monomer.

If only 1% of the present one gram polymerizes, the quantity of the developed heat will be:

$$Q_{1\%,1g} = \frac{H}{100M} \qquad (2)$$

and for G grams it will be

$$Q_{1\%,G} = \frac{HG}{100M} \qquad (3)$$

In a general case for the polymerization rate of R (%/h), and with the introduction of the conversion factor 3.6 to convert joules per mol into miliwatts, the power W generated in one hour is given by

$$W = \frac{HGR}{360M} \qquad (4)$$

The calibration of the calorimeter has shown that the power of 1mW generates a signal of 65 microvolts. Multiplying Equation 4 by this calibration factor one gets an expression for the voltage signal S:

$$S = \frac{65HGR}{360M} \qquad (5)$$

Therefore, the reaction rate can be calculated from the recorded signal S by using the equation:

$$R = \frac{360MS}{65HG} \qquad (6)$$

Other characteristics of the calorimeter as well as a more detailed description can be found elsewhere.[4]

Point-by-point methods

Several samples of styrene were allowed to polymerize spontaneously at different times. At appropriate intervals, in the range of 10-260 hours, polymerization was interrupted and the polymer content in the samples was determined by 3 different methods as described below.

Refractometry

Immediately after the removal of the sample from the thermostated bath, the refractive index n_D was measured by an Abbe refractometer using the monochromatic D line of the sodium spectrum. The percentage of polystyrene in the sample was calculated from the increase of this index compared to its value for pure styrene.

Gravimetry

The sample was dissolved in benzene and polystyrene was precipitated by adding of methanol. The precipitate was washed, dried and weighed.

Photometry

The concentration of the residual monomer was determined by the ultraviolet absorption method[6] based on the linear dependence of optical density on styrene concentration at 281nm, 288nm and 290nm.

Table 1 gives the comparison of conversions to polymer in the case of spontaneous polymerization of styrene obtained by calorimetry and by other methods (gravimetry, photometry and refractometry). In the case of calorimetry the conversion was determined by integration of the heat flow rate vs. time curve.

TABLE 1 - Spontaneous Styrene Polymerization at 90.15 °C

Reaction time, h	Conversion to polymer as obtained by			
	Calorimetry, %	Gravimetry, %	Refractometry, %	Photometry, %
10	8.85	9.1	8.7	-
20	17.55	17.3	17.6	-
30	26.00	26.3	25.7	-
36	32.8	32.3	-	-
40	34.8	34.8	35.0	-
50	43.5	43.6	-	-
80	67.9	67.1	-	68.0
120	87.4	-	-	87.6
160	94.3	-	-	94.0
260	96.3	-	-	96.2

Agreement between the various methods is excellent but nevertheless, calorimetry possesses great advantages:

(1) It directly measures the rate of reaction at every moment, while most of the other methods used so far offer only indirect approach for obtaining the polymerization rate from conversion vs. time relation.

(2) Calorimetry continuously records the reaction rate with only one sample for the whole conversion range and is independent from the physical state of the reaction system. Dilatometry, which is the most widely used method for investigation of polymerization kinetics, is limited to moderate conversions and is not suitable for viscous or solid systems or high temperatures. Refractometry is applicable in some cases but only for lower conversion. Photometry is applicable for determination of residual monomer at very high conversions. Point-by point gravimetry can be used in broad conversion ranges, but accuracy in determining the polymerization rate by this method is poor.

(3) The sensitivity and accuracy of calorimetry is better than those achieved by any other method.

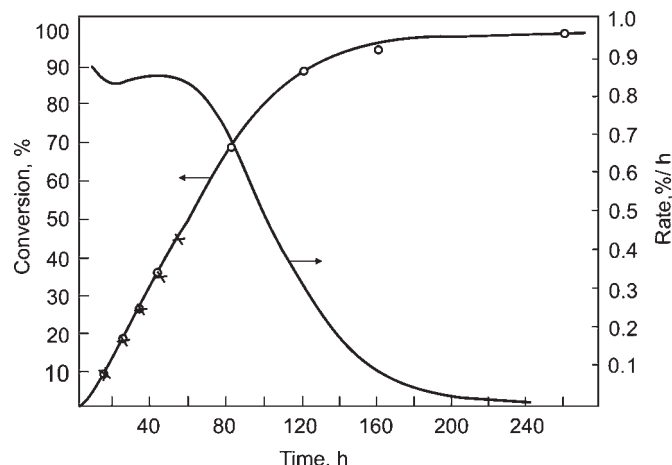These advantages of calorimetry are clearly illustrated in Figure 1.

FIGURE 1 – Dependence of reaction rate and conversion on reaction time in spontaneous polymerization of styrene at 90.15°C (calorimetry – full line, gravimetry - ×, photometry - O, refractometry - ●)

If we try to derive the polymerization rate from conversion vs. time curve with good fitting of experimental points on the curve from all methods used, we are inclined to believe that the polymerization rate is constant up to 60% of the conversion. It causes more doubts when scattering of results is higher as is usually the case.

However, calorimetry clearly shows that the polymerization rate changes with time; it decreases from the beginning to about 20% of the conversion and then increases to the maximum at 45% and decreases again at higher conversions. The increase of the polymerization rate after 20% of the conversion is caused by the decrease of the termination rate due to the increase of viscosity of the system with conversion, i.e. by the gel-effect. The gel-effect is not very pronounced in the spontaneous polymerization of styrene and could not be easily detected by other methods. Thus, only calorimetry made it possible to obtain fine details of the complete kinetic curves.

The calorimeter we used makes stable and accurate measurements possible over a period of several weeks. Its resolution at isothermal conditions is 50mW and 0.18 J/h respectively. Since the heat of polymerization of liquid styrene monomer is equal to 72 811 J/mol[7] at 90.15°C we can conclude that 1g of styrene will develop 649J. The rate of heat production equal to the resolution of our instrument (0.18 J/h) corresponds to the polymerization rate of 0.00026g/h. When working with 10g of styrene (a quantity which is easily handled) the polymerization rate of 0.00026g/h corresponds to 0.0025% of the monomer sample. In other words, when the rate of styrene polymerization is measured, the resolution of 0.0025% can easily be achieved, which is by far better from that which can be obtained by other methods.

On the basis of the presented results we point out that Calvet microcalorimetry is a very promising method for investigating the kinetics of polymerization.

Graft polymerization

Radiation graft polymerization is one of the methods to improve the properties of polymers. It has been studied extensively with many systems.[8,9] In most publications kinetic curves constructed on the basis of gravimetrically obtained individual points are presented. Apart from the sources of error generally inherent to this method, in graft polymerization deviations caused by different properties of individual samples have to be taken into account, too. Thus, the reproducibility of the experiments is low and in some cases even the qualitative observation of the course of reaction becomes uncertain. Some improvement was made by applying dilatometry to some grafting systems,[10] but the applicability of this method is strongly limited because of the bubble formation around the films during the polymerization.

To obtain the details of the graft polymerization kinetics we used an adapted Calvet-type microcalorimeter for investigation of grafting of styrene and methylmethacrylate on air-preirradiated polyethylene.[11]

Low density polyethylene (LDPE) with the commercial name *LUPOLEN 1810 H* and high density (HDPE) type *LUPOLEN 5041 D* in 0.1mm thickness were used.

Extracted polyethylene films were irradiated in the air at room temperature with ^{60}Co gamma rays. The dose rate was 16 Gy/h and total doses 6-20 kGy. Irradiated polyethylene was used either immediately after irradiation or after different storage periods (up to 11 weeks).

Weighted and preirradiated polyethylene films were immersed in purified monomer in reaction tubes and connected to a vacuum line, evacuated and sealed off under vacuum.

Reaction took place either in thermostated water bath at 60°C or in the Calvet microcalorimeter at 40°C, 60°C and 80°C, respectively.

In the first case the extent of grafting was determined gravimetrically by soaking the grafted films in benzene followed by drying at 55°C – 60°C under reduced pressure (water jet pump) to constant weight and calculated as the per cent weight gain. Since the recorded calorimetric signal vs. time curve is proportional to the grafting rate at any moment the grafting yield in calorimetrically followed reaction was obtained by the integration of the area under this curve.

Styrene-Polyethylene

Figure 2 shows the gravimetrically (curve 2) and calorimetrically (curve 1) obtained conversion curves at 60°C for styrene polymerization in the presence of air-preirradiated polyethylene. It should be remembered that the calorimeter measures, just like a dilatometer, the sum of all polymerization processes going on inside the sample. At the given temperature the correction for the rate of thermal polymerization of styrene has been made. Heat effects produced by possible structural changes in polyethylene during the grafting could be neglected. Accordingly, calorimetrically obtained conversion curves represent the sum of grafting yield and the yield of homopolymerization of styrene initiated by active centres present in the polyethylene films. The difference between calorimetrically and gravimetrically obtained conversion corresponds to the amount of homopolymer formed.
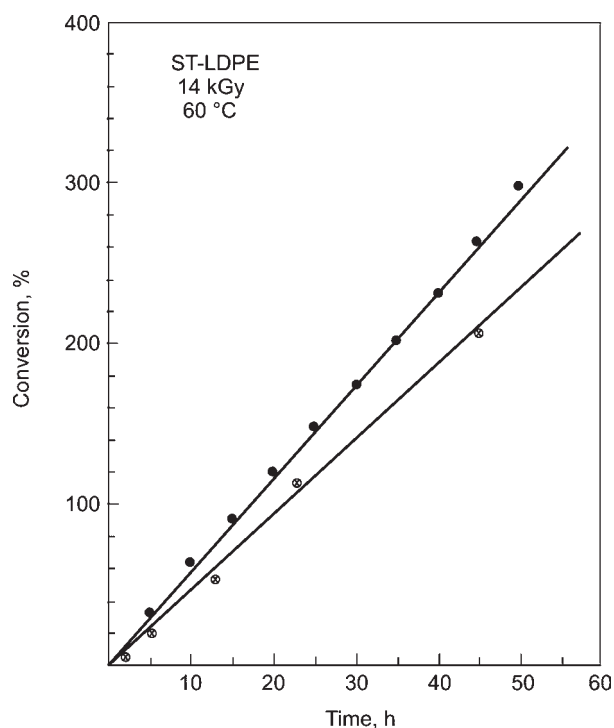

FIGURE 2 – Graft polymerization conversion curves obtained by calorimetry (curve 1) and gravimetry (curve 2)

In most of the published investigations linear conversion curves were reported for the wide initial stage of grafting onto air-preirradiated polyethylene thus indicating the constant rate of polymerization.

On the basis of the following experimental facts: for equal initiation rates the rate of grafting is higher in thicker films; grafting rate is higher in high density polyethylene compared to low density polyethylene and the swelling rate of polyethylene by styrene is higher than the rate of grafting, we have shown in a previous paper[12] that at the given experimental conditions, for 0.1mm thick polyethylene films, the propagation reaction is not controlled by diffusion of styrene into polyethylene film.

The instantaneous rate of polymerization measured by calorimetry gives the possibility to obtain fine structure of kinetic curves. As can be seen in Figure 3 in the case of low density polyethylene the rate of polymerization decreases in reality slowly in time reaching approximately a constant value and then increases again. There could be two reasons for decreasing of polymerization rate over time: a) concentration of active centres decreases, b) with increasing grafting yield swelling is more rapid and stronger, thus the viscosity of the reaction medium decreases, i.e. termination rate increases and overall polymerization rate decreases. It was not possible to distinguish which of the two effects dominates.
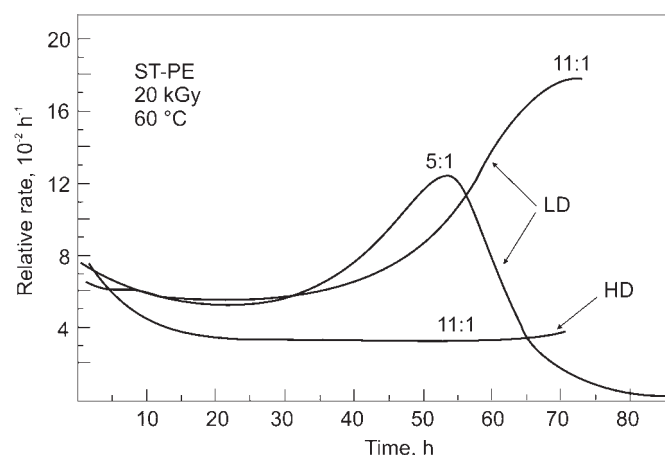

FIGURE 3 – Dependence of graft polymerization rate on type of polyethylene and weight ratio styrene - polyethylene

The increase of the polymerization rate with time which follows in the case of prolonged reaction could be caused by the increase of viscosity, but the structural changes in films and new initiation sites from crystalline parts would increase the reaction rate as well.

In order to distinguish between the two possibilities we investigated the effects of monomer to polymer ratio on the shape of curves. Obviously smaller quantity of monomer (curve 5:1) gets exhausted more rapidly; the polymerization rate increases earlier but its maximal value is lower. This experimental fact proves that the increase of viscosity in the system plays a decisive role, i.e. the termination reaction is in most cases in the grafting reactions diffusion-controlled.

The maximal reaction rate in the early stage of reaction and steep decrease down to approximately constant low rate in high density polyethylene suggests two types of active species: peroxy radicals reacting at the beginning and peroxides decomposing slowly in the course of reaction. Accordingly, in low density polyethylene the concentration of peroxides is much higher and they have the dominating role in the initiation process.

Methylmethacrylate-Polyethylene

Figure 4 shows the kinetic curves for graft polymerization of methylmethacrylate in the presence of high density polyethylene at 40°C, 60°C and 80°C. The maximal rate of polymerization observed at the beginning of reaction at 60°C and 80°C is in agreement with the assumption that peroxy radicals take part in reaction mainly at the beginning and after their exhaustion approximately constant rate of polymerization initiated by the decomposition of peroxides is established.
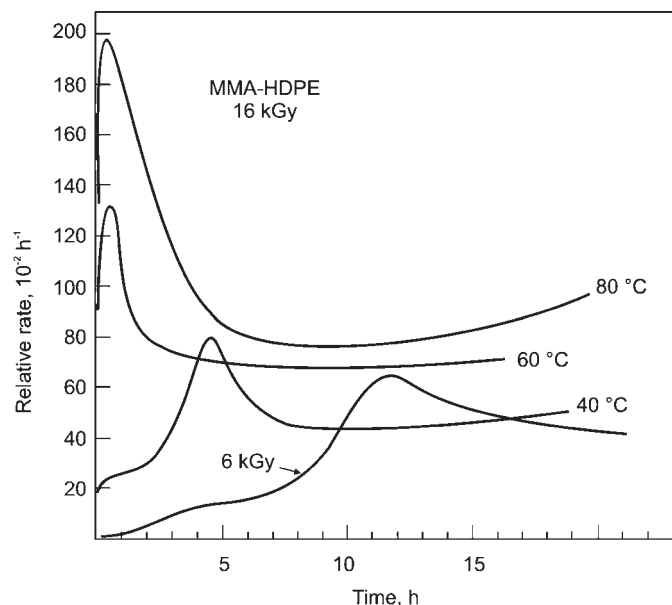
FIGURE 4 - Dependence of graft polymerization rate of methylmethacrylate on high density polyethylene on temperature and preirradiation dose

At 40°C polymerization rate increases slower reaching maximum after some time when the progress of grafting and swelling at this temperature have made the most of free radicals accessible and then again decreases until constant rate.

For lower preirradiation doses grafting yield is lower, swelling is slower and weaker, too, and it takes more time to make all radicals accessible for grafting, which means that at 40°C structural factors influence the kinetics of the reaction.

Figure 5 shows the kinetic curves for graft copolymerization at 60°C of methylmethacrylate on high density polyethylene stored after irradiation at room temperature for various periods of time. It can be seen that after one week of storage at room temperature the concentration of radicals is still high in polyethylene films which results in higher polymerization rate at the beginning of the reaction. Concentration of radicals decreases as storage time increases and after 11 weeks of storage practically all radicals have decayed. When graft polymerization is performed at 40°C (Figure 6) the structural factors determine the rate of reaction at the beginning, their influence being higher as the concentration of active centres decreases with storage.
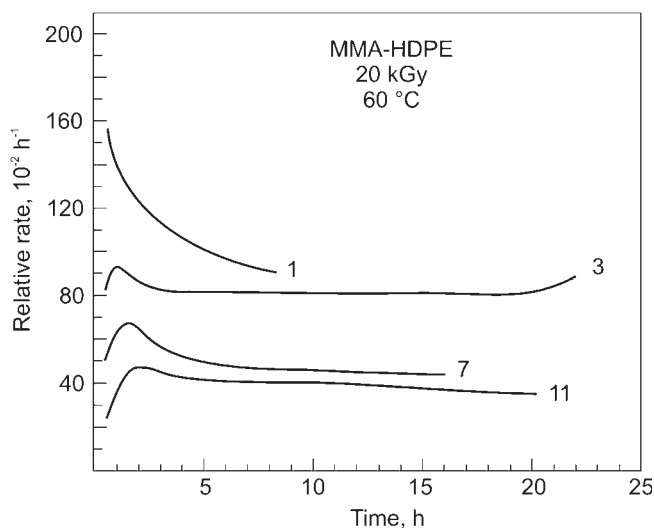

FIGURE 5 - Dependence of graft polymerization rate at 60°C on storage time of preirradiated polyethylene (1, 3, 7 and 11 weeks)
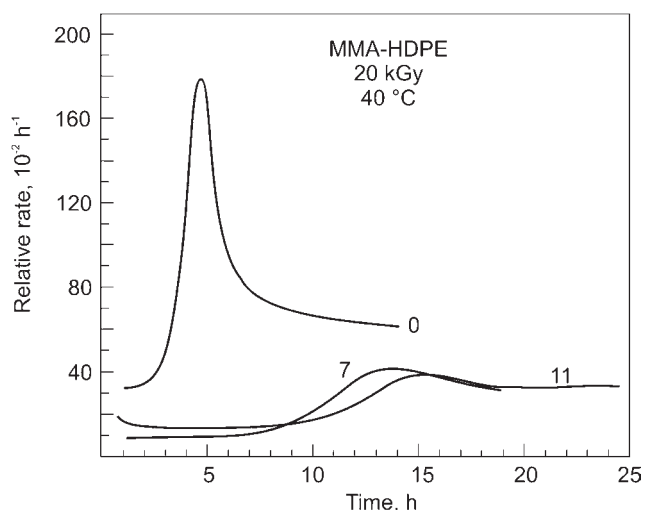

FIGURE 6 - Dependence of graft polymerization rate at 40°C on storage time of preirradiated polyethylene (0, 7 and 11 weeks).

High conversion copolymerization

The major advantage of the calorimetry over the point-by-point method widely applied in investigation of the kinetics of polymerization is the high reproducibility of experiments and the possibility to measure reaction rate continuously up to high conversion. Especially, successful was the application of the calorimetry in our investigation of the copolymerization reactions[13-23] with emphasis on the alternating copolymerization.

A typical example is high conversion copolymerization of α-methylstyrene (α-MeSt) with n-phenylmaleimide (NPhMI). This copolymerization is slow and convenient to be followed by Calvet microcalorimeter.

Figure 7 shows the rates and conversions of copolymerization at 60 °C of α-MeSt with NPhMI in toluene at different ratios of comonomers in the feed. The reaction was initiated with AIBN. At equimolar 1 to 1 ratio of comonomers (Figure 7a) after the system reaches thermal equilibrium (about 10 minutes after putting the sample in calorimeter) the reaction proceeds with maximal rate and then the rate decreases slowly with time approaching zero. Gravimetric determination of the quantity of obtained polymer as well as integration of the area under calorimetric curve indicated near 100% conversion of comonomers. Elemental analysis as well as ^{1}H and ^{13}C NMR analysis proved that alternating copolymer was obtained.

The most interesting results were obtained in calorimetric following the copolymerization of the same comonomers at nonequimolar ratios in the feed (Figure 7b,c,d,e,f). At the molar ratio 0.1 α-MeSt to 0.9 NPhMI (Figure 7b) initial maximal reaction rate decreases with reaction time reaching minimum value after one hour and then increases again until the maximum much higher than was the initial maximal rate and then again decreases slowly approaching zero value.

At the molar ratio 0.2 α-MeSt to 0.8 NPhMI (Figure 7c) the minimum was observed after 2.5 hours and the rate at the second maximum was not much higher than the initial rate.

At the molar ratio 0.4 α-MeSt to 0.6 NPhMI (Figure 7d) a minimum was observed after 7.2 hours and the rate at the second maximum was much lower than the initial rate.

It should be pointed out that the experimentally determined conversions at all the observed minima closely correspond to the theoretically possible yield of alternating copolymers (Table 2). Since α-MeSt does not homopolymerize under the applied experimental conditions copolymerization stops after the theoretical yield of alternating copolymer is reached in the case of an excess of α-MeSt (Figure 7e,f, Table 2).
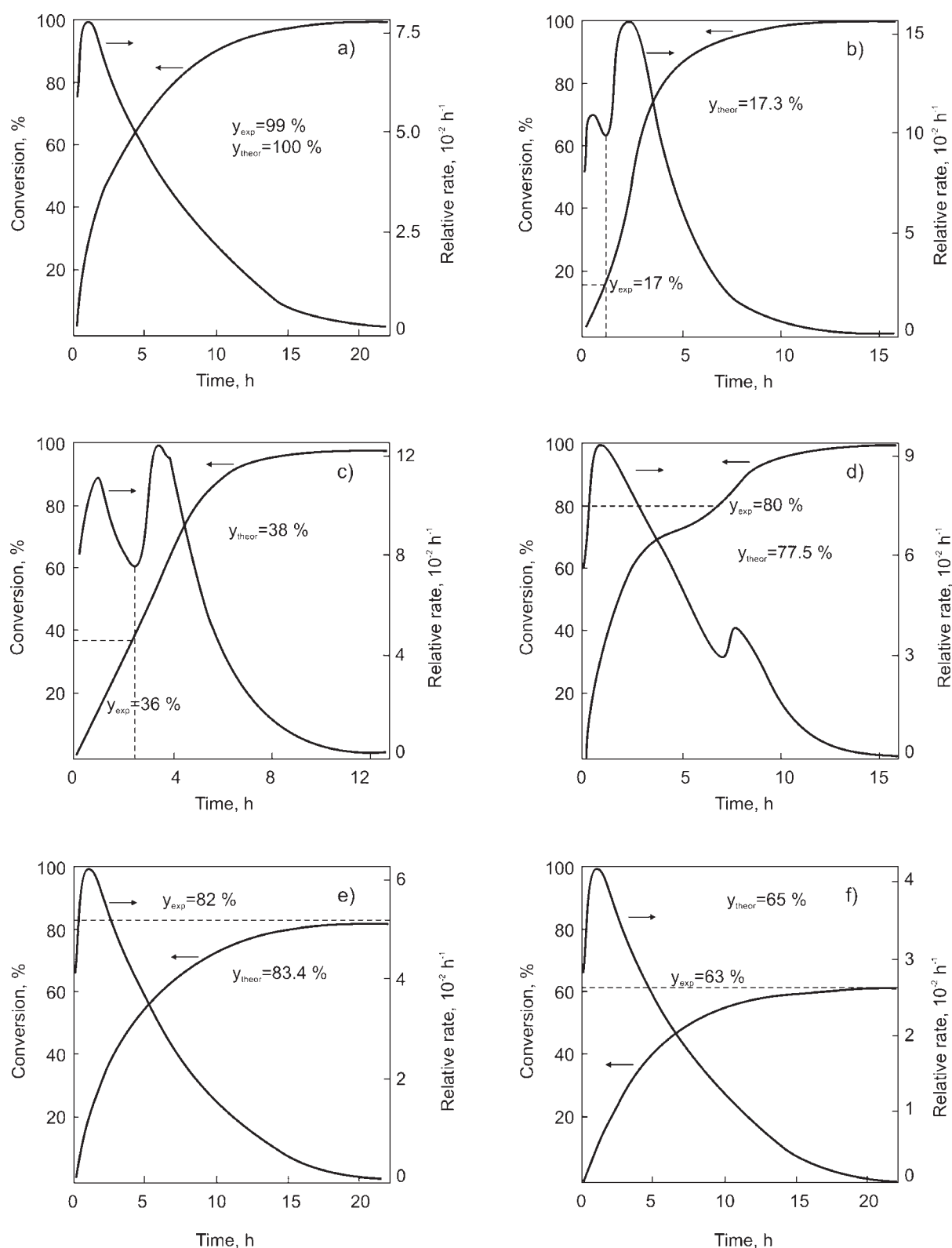
FIGURE 7 – Dependence of reaction rate and conversion on time in the copolymerization of α-MeSt with N-PhMI at molar ratios: a) 0.5 to 0.5; b) 0.1 to 0.9; c) 0.2 to 0.8; d) 0.4 to 0.6; e) 0.6 to 0.4; f) 0.7 to 0.3; in toluene at 60°C; 0.3% AIBN; total monomer concentration 2 mol/dm³. (y_{theor} = theoretical yield of alternating copolymer, y_{exp} = experimentally determined yield of alternating copolymer)

Similar data were also obtained in the copolymerization of α-MeSt with maleimide and with N-methylmaleimide at various ratios of electron donor and electron acceptor monomers in the feed. Wide strong evidence was obtained that the theoretical yields of alternating copolymers are in good agreement with the experimental data, thus indicating that alternating copolymerization of α-MeSt with maleimide, N-methylmaleimide or N-phenylmaleimide and homopolymerization of homopolymerizable electron acceptor monomers are not simultaneous but are consecutive reactions – homopolymerization starts only after the completion of alternating copolymerization. Calorimetric measurements also show that the rate of alternating copolymerization of α-MeSt with MI, at equimolar ratio of comonomers and the rate of homopolymerization of MI are not significantly different. Similar was also found in the

TABLE 2 - Comparison of experimental and theoretical conversion of alternating copolymer of α-MeSt with N-Phenilmaleimide at 60°C in toluene; 0.3 wt% AIBN; total monomer concentration 2 mol dm^{-3}

Molar ratio		Conversion of alternating copolymer, %	
α-MeSt	N-PhMI	Experimental	Theoretical
0.5	0.5	99	100.0
0.1	0.9	17	17.3
0.2	0.8	36	38.0
0.4	0.6	80	77.5
0.6	0.4	82	83.4
0.7	0.3	63	65.0

copolymerization and homopolymerization of α-MeSt with NMeMI or NPhMI thus indicating that alternating copolymerization prior to homopolymerization cannot be explained due to the difference of the rate of copolymerization and homopolymerization reaction. It is well known that α-MeSt as a strong electron donor forms stable charge-transfer complexes with electron acceptors like maleimides. Thus, the competitive character of the copolymerization and homopolymerization reaction can be explained as a consequence of the participation of the charge-transfer complex in the copolymerization reaction, which agrees with the assumption of Shirota and coworkers.[24,25] Our detailed studies on the mechanism of alternating copolymerization of α-MeSt with NPhMI and NMeMI provide evidence that the rate of formation of α-MeSt free radicals is much faster than the rate of formation of electron acceptors free radicals. Since in all cases alternating copolymer are formed regardless of ratio of comonomers in the feed, it indicates that the addition of α-MeSt is preferentially done through charge-transfer complex, and as long as α-MeSt is present in the feed alternating copolymers are formed through the addition of charge-transfer complex. Only after α-MeSt disappears from the reaction mixture the free radical initiation of electron acceptor starts. Very interesting results were also obtained in calorimetric investigation of copolymerization of α-MeSt with N-alkylmaleimides (RMI; R=Et, n-Pr, iso-Pr, n-Bu, n-Hex). In the presence of an excess of homopolymerizable RMI, alternating copolymers are quantitatively formed prior to the formation of poly(RMI) indicating the participation of charge-transfer complex. The equilibrium constants of charge-transfer complexes were not significantly dependent on steric factors but the rate of copolymerization of α-MeSt with RMI was largely influenced by the bulkiness of alkyl groups.

Conclusions

An adapted Calvet microcalorimeter was used to follow the course of spontaneous polymerization of styrene at 90.15°C. Comparative investigations with widely used point-by-point methods refractometry, gravimetry and photometry have been performed. The agreement between results of various methods was excellent but calorimetry features great advantages: it directly measures the rate of reaction, continuously records reaction rate with only one sample up to high conversion and is independent of the change of physical state of the reaction system. The sensitivity and accuracy of calorimetry is better than achieved by other methods. Thus, only calorimetry made it possible to obtain fine details of the complete kinetic curves and observe the gel-effect which is not very pronounced in the spontaneous polymerization of styrene and could not be easily detected by other methods.

In calorimetric investigation of grafting of styrene and methylmethacrylate on polyethylene preirradiated in air unknown kinetical details were observed. The difference in reaction kinetics with low and high density polyethylene has been explained in terms of different mechanisms of reaction, i.e. by initiation of grafting by peroxides and peroxy radicals. In low density polyethylene concentration of free radicals was negligible to that of peroxides and peroxides

have a dominating role in the initiation. The effect of monomer to polymer ratio on reaction showed that the change of viscosity of the system plays an important role. The decay of active species (formed by preirradiation of polymer) in time can be followed by this method as well.

Calorimetric investigation provided strong evidence that in copolymerization of α-methylstyrene with maleimides, regardless of ratio of comonomers in the feed only alternating copolymer is formed as long as both comonomers are present in the feed. Only after α-MeSt disappears from the reaction mixture the homopolymerization of maleimides starts. It indicates that the addition of α-MeSt is preferentially done through charge-transfer complex. The equilibrium constants of charge-transfer complex were not significantly dependent on steric factors but the rate of copolymerization of α-MeSt with n-alkilmaleimides was largely influenced by the bulkiness of alkyl groups.

REFERENCES

1. Horie, K., Mita, I., Kanabe, H.: *Calorimetric investigation of polymerization reactions. I. Diffusion-controlled polymerization of methyl methacrylate and styrene.* J. Polym. Sci. A-1(1968)6, 2663-2676.

2. Ebdon, J. R., Hunt, B.: *Study of the free-radical polymerization of styrene by differential scanning calorimetry.* J Anal. Chem. 45(1973), 804-806.

3. Ranogajec, F., Barić, M., Dvornik, I., Dobo, J.: *Calorimetric investigation of thermal polymerization of styrene.* Preprints XXIII Intern. Symp. on Macromolecules, Madrid, 1(1974), 1-3.

4. Barić, M. *Microcalorimetric Investigation of Polymerization Processes*, Ph.D. Thesis, Universtiy of Zagreb, 1975.

5. Barić, M., Ranogajec, F., Dvornik, I.: *Calvet microcalorimetry - a new suitable method for investigation of polymerization reactions.* Croat. Chem. Acta 52(1979), 61-65.

6. Luce, E. N.: *Analysis of Styrene Monomer*, in: R. H. Boundy, R. F. Boyer, and S. M. Stoesser, (EDs), *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold Publ. Corp., New York 1952, 185-188.

7. Stull, D. R.: *Physical Properties of Styrene Monomer*, in: R. H. Boundy, R. F. Boyer, and S. M. Stoesser, (EDs), *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold Publ. Corp., New York 1952, 77-78.

8. Chapiro, A.: *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.

9. Ceresa, R. J. (Ed.): *Block and Graft Copolymerization*, Interscience, New York, 1976.

10. Dobo, J., Czvikovszky, T., Ranogajec, F.: *Direct radiation and spontaneous grafting of styrene on polyolefins.* Proc. Second Tihany Symp. on Rad. Chem., Akademiai Kiadó, Budapest, 1967.

11. Ranogajec, F., Dvornik, I., Dobo, J.: *The effect of the type of polyethylene on the grafting of styrene on polyethylene. I. Direct radiation grafting and grafting by preirradiation in vacuo.* Eur. Polym. J. 6(1970), 1169-1177.

12. Barić, M., Ranogajec, F., Dvornik, I.: *Calorimetric investigation of grafting of styrene and methylmethacrylate onto air-preirradiated polyethylene.* Croat. Chem. Acta 52(1979), 223-231.

13. Ranogajec, F., Vuković, R., Fleš, D.: *Radiation-induced copolymerization of phenylvinyl alkyl ethers and maleic anhydride.* J. Polym. Sci. 22(1984), 41-47.

14. Fleš, D. D., Vuković, R., Ranogajec, F*.: Copolymerization of alpha-methyl-styrene and N-phenylmaleimide*. J. Polym. Sci. Polym. Chem. Ed. 27(1989), 3227-3236.
15. Ranogajec, F., Fleš, D. D., Vuković, R., Fleš, D.: *High-conversion polymerization of alpha-methylstyrene and maleimide at different monomer-to-monomer ratios in feed.* Polym. Bull. 24(1990), 597-602.
16. Fleš, D., Vuković, R., Ranogajec, F., Fleš, D. D.: *High conversion copolymerization of α- methylstyren with N-methykmaleimide or N-phenylmaleimide*. J. Makromol. Sci. - Chem. (1990)A27, 1621-1630.
17. Janović, Z., Ranogajec, F., Kučišec-Dolenc, J.: *Copolymerization and copolymers of N-(2,4,6-tribromphenyl)maleimide with styrene*. J. Makromol. Sci. (1991)A28, 1025-1037.
18. Janović, Z., Matusinović, T. T., Ranogajec, F.: *Alternative copolymerization of styrene and N-(-4-bromophenyl) maleimide*. J. Makromol. Sci. (1992)A29, 801-811.
19. Ranogajec, F., Fleš, D. D., Hace, D., Vuković, R.: *Copolymerization of α-methylstyrene with N-alkylmaleimides.* Polym. Bull. 28(1992), 319-325.
20. Fleš, D., Hace, D., Ranogajec, F., Vuković, R.: *Copolymerization of α-methylstyrene with 4'-N-(benzo-15-crown-5) maleimide.* Polym. Bull., 29(1992), 153-157.
21. Janović, Z., Matusinović, T., Ranogajec, F.: *Copolymerization and copolymers of N-(2,4,6-tribromphenyl) maleimide with methyl acrylate and methyl methacrylate.* Macromol. Chem. 194(1993), 1915-1923.
22. Fleš, D. D:, Hace, D., Ranogajec, F., Vuković, R., Fleš, D.: *The application of Taft-Hancock steric constants to the free-radical initiated copolymerization of N-alkylmaleimides with α-methylstyrene.* Polym. Bull. 33(1994), 445-449.
23. Vuković, R., Kurešević, V., Srića, V., Fleš, D., Ranogajec, F.: *Copolymerization of 2-vinylnaphthalene with benzylidenemalononitrile*. J. Macromol. Sci. - Pure Appl. Chem. 12(1994)A31, 2001-2010.
24. Shirota, Y., Yoshimura, M., Matsumoto, A., Mikawa, H. *: Mechanism of charge-transfer polymerization. VI. Alternating radical copolymerization of N-vinylcarbazole with electron-accepting monomers*. Macromolecules, 7(1974), 4-11.
25. Yoshimura, M., Nogami, T., Yokoyama, M., Mikawa, H., Shirota, Y.: *Studies on the mechanism of alternating radical copolymerization. quantitative treatment of the initial copolymerization rate*. Macromolecules, 9(1976), 211-213.

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Vijesti

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Pad i rast tržišta polietilena

Gospodarska kriza donijela je promjene i na tržište polietilena, pri čemu je 2008. bila posebno krizna godina. U Sjevernoj Americi potražnja za PE-LLD-om smanjila se za više od 7 %, za PE-HD-om više od 8 %, a za PE-LD-om čak 11 %. Čak je i veliko kinesko tržište osjetilo pad od 5 %, no veći pad na američkom tržištu znači da je Kina prvi put postala najveći svjetski potrošač polietilena.

Niže cijene polietilena, zbog slabije potražnje i niskih troškova energije, potencijalno mogu stimulirati potražnju i privući kupce na tržište. Rast *srednje klase* u Indiji i Kini također će bitno pridonijeti oporavku polietilena. Kada se tržište oporavi, predviđa se globalni porast potražnje za polietilenom od 4,2 % između 2008. i 2013.

Predviđa se da će se tržište polietilenskih proizvoda početi oporavljati tijekom 2009. Do 2011. potražnja za polietilenom za rotacijsko kalupljenje rast će 6 % godišnje, a potražnja za polietilenom za injekcijsko prešanje, filmove i folije, cijevi i profile oko 5 % godišnje.

Globalno, očekuje se pad proizvodnje polietilena na oko 75 % dosadašnje proizvodnje do 2010., a to će stanje utjecati na sve osim na Bliski istok. Tako tvrtka *Borouge* i dalje proširuje svoje pogone za proizvodnju poliolefina u Abu Dhabiju. Povećanje kapaciteta od 2,5 milijuna tona godišnje bit će dovršeno u posljednjem tromjesečju 2013. (projekt *Borouge* 3). Proširenje će tvrtki

Borouge, koja je zajednički pothvat nacionalne naftne tvrtke iz Abu Dhabija *ADNOC* i tvrtke *Borealis*, omogućiti da zadovolji sve veću potražnju za polietilenom i polipropilenom na tržištima Bliskog istoka i Azije.

Sadašnji projekt *Borouge* 2 povećat će kapacitet proizvodnje tvrtke tri puta (na oko 2 milijuna tona godišnje), a bit će dovršen 2010. Projekt *Borouge* 3 uključuje konstrukciju postrojenja za krekiranje etana te postrojenja za proizvodnju polietilena i polipropilena druge generacije *Borstar*, postrojenje za proizvodnju PE-LD-a i postrojenje za proizvodnju butena. Do kraja 2013. proizvodni kapacitet tvrtke trebao bi iznositi 4,5 milijuna tona godišnje.

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Hoće li se ostvariti nepovoljne prognoze?

Prema prognozama *Assocomaplasta*, udruženja oko 200 talijanskih proizvođača opreme za preradbu plastike i gume, 2009. godina za tu će industriju biti nepovoljna. Trend sniženja prihoda na domaćem i stranim tržištima počeo je još u 2008. godini, a u 2009. bi se trebao nastaviti. Ukupna vrijednost najavljene proizvodnje je 3,8 milijardi eura. Od toga na izvoz ide 2,3 milijarde, a na domaćem se tržištu planiraju realizirati 2 milijarde eura. Uz predviđeni uvoz ovoga industrijskoga segmenta od 500 milijuna eura još ostaje znatan doprinos suficitu talijanske vanjskotrgovačke bilance od 1,8 milijardi eura.

Najveće smanjenje osjeća se u narudžbama ubrizgavalica i kalupa, koje bi moglo iznositi i do 20 %. Silazni trend u tom području osjetio se još u jesen 2008. godine.

Assocomaplast Press Release, veljača 2009.

Održiva proizvodnja u kriznim vremenima

Sabicova nova tvornica polietilena visoke gustoće u njemačkome Geisenkirchenu, nazvana *LD6*, počela je s proizvodnjom početkom 2009. Na tržište isporučuje materijal *Vistolen A*, namijenjen proizvodnji cijevi. Puštanjem u rad te tvornice na tržištu je osigurana dovoljna količina materijala čija primjena omogućuje inovativna rješenja gotovih proizvoda uz istodobno za okoliš povoljniji proizvodni postupak.

Održivost je, prema riječima poslovnoga direktora te tvornice, i u ovim teškim vremenima na prvome mjestu. Izgradnjom nove tvornice postignut je optimalan odnos između poslovnih koristi i održive proizvodnje.

U novoj su tvornici sniženi proizvodni troškovi, povećana je proizvodnost i iskorištenje resursa. U usporedbi s konvencionalnom proizvodnjom PE-HD-a, u ovoj je omogućena ušteda energije od 8 % uz istodobno smanjenje opterećenja okoliša.

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