

Calorimetric Investigation of Grafting of Styrene and Methylmethacrylate onto Air-Preirradiated Polyethylene

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All 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 graft copolymerization reactions in which the accuracy of measurement could be affected even by the different properties of individual polymer samples.

In this work a new method, calorimetry, free of mentioned disadvantages is generally proposed for investigation of polymerization processes and particularly its application to radiation induced grafting of styrene and methylmethacrylate onto polyethylene is demonstrated.

Experimental results showed the possibility of calorimetry to measure the grafting rate continuously and directly in the whole conversion range with the accuracy much better than with any other method used so far.

It was concluded that styrene grafting is non-diffusion-controlled, whereas methylmethacrylate grafting is not diffusion-independent. With both monomers the reaction kinetics was found to be dependent on the type of polyethylene as a consequence of different mechanisms, i. e. in the initiation step two different species, peroxy radicals and peroxides, take part. Its concentration is different in two types of polyethylene used. In the case of high density polyethylene both active species participate in the initiation process equally, according to their different nature. However, in low density polyethylene the concentration of peroxy radicals is negligible compared to that of peroxides and therefore peroxides have dominating role in the initiation step of grafting reaction. The change of the viscosity of reaction medium in the course of reaction as well as the structure of polymer in the case of high density polyethylene influence the kinetics of grafting reaction.

INTRODUCTION

Graft copolymerization is one of the methods used to improve the properties of polymers. It has been studied extensively with many systems^{1,2}. 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 copolymerization deviations caused by the different properties of individual samples have to be taken into account,

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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 systems³, but the applicability of this method is strongly limited, because of the bubble formation around the foils during the polymerization.

To obtain the details of the graft copolymerization kinetics we used an adapted Calvet-type microcalorimeter for investigation of grafting of styrene and methylmethacrylate to air-preirradiated polyethylene.

EXPERIMENTAL

Materials

Polymer. — Polyethylene foils were supplied by BASF, Ludwigshafen. Low density polyethylene (LDPE) with the commercial name LUPOLEN 1810 H and high density (HDPE) type LUPOLEN 5041 D in 0.1 mm thickness were used. LDPE had a density of 0.918 g/cm³, degree of branching of 30 CH₃ groups per 1000 carbon atoms and melt flow index of 1.7 g/10 min, whereas HDPE was characterized by respective values: 0.950 g/cm³, 5 CH₃/1000 C and 0.2 g/10 min.

In order to eliminate additives and stabilizers polyethylene foils in form of strips with approximate dimensions 5 × 50 mm were extracted for 48 hours with the boiling mixture benzene-ethanol 1 : 1. After extraction the strips were dried at 55 °C and reduced pressure (water jet pump) to constant weight. So prepared polymer samples were afterwards stored in a dark place at room temperature.

Monomers. — Analytical grade styrene supplied by Merck-Schuchardt, Darmstadt, was freed of inhibitor by washing three times with 10% NaOH solution and then with distilled water until the washings were neutral, dried with CaCl₂ and then distilled in nitrogen atmosphere at 52 °C using water jet pump. The middle fraction is preserved and stored before the use in a refrigerator.

Analytical grade methylmethacrylate was also supplied by Merck-Schuchardt. Purification procedure was the same as applied to styrene.

Irradiations

Extracted polyethylene foils were irradiated in the air at room temperature with ⁶⁰Co gamma rays at the irradiation facility⁴. Dose rate was 1600 rad/h and total doses 0.6–2.0 Mrad. Irradiated polyethylene was used either immediately after irradiation or after different storage periods (up to 11 weeks).

Grafting Procedure

Weighed and preirradiated polyethylene foil samples were immersed in purified monomer in reaction tubes and connected to a vacuum line. Monomer to polymer weight ratio varied from 5 : 1 to 11 : 1 in the case of styrene, and from 9 : 1 to 170 : 1 in the case of methylmethacrylate grafting.

Oxygen was removed by freezing the polymer-monomer mixture and evacuation to 10⁻⁵ mm Hg* followed by thawing. Freezing — thawing cycle was repeated three times before reaction tubes were 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 foils 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.

Calvet Microcalorimeter

The calorimeter is working with two compensated cells situated in a thermostated metal block. Each cell is surrounded by 496 thermocouples. In the set-up used in the

* 1 mm Hg ≈ 133.322 Pa.

present work, it is capable of the continuous recording of 5 mW power developed in one of the cells with a precision of 1%. The stability in measuring the given power at constant temperature could be assured over several weeks.

The power P (mW) generated by the polymerization is given by the equation⁵:

$$P = \frac{H R G}{86 M_w}$$

where H = heat of polymerization of monomer, in cal/mol

M_w = molecular weight of monomer

R = rate of polymerization, in %/h

G = weight of monomer, in grams

RESULTS AND DISCUSSION

Styrene-Polyethylene

In Figure 1 gravimetrically (curve 2) and calorimetrically (curve 1) obtained conversion curves at 60 °C for styrene polymerization in the presence of air-preirradiated polyethylene are shown. It should be remembered that the calorimeter measures, just like a dilatometer, the sum of all polymerization processes going on inside the sample. At 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

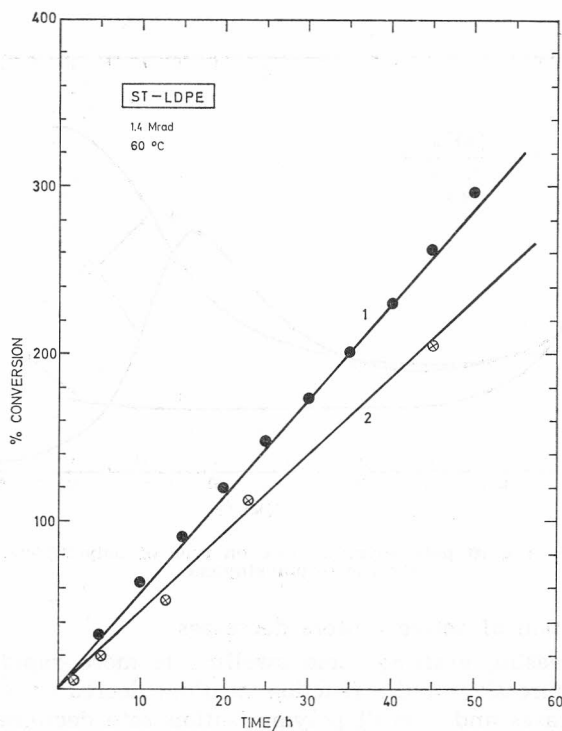


Figure 1. Graft polymerization conversion curves obtained by calorimetry (curve 1) and gravimetry (curve 2).

styrene initiated by active centers present in the polyethylene foils. The difference between calorimetrically and gravimetrically obtained conversion corresponds to the amount of homopolymer formed.

In most of 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:

- (i) for the equal initiation rates the rate of grafting is higher in thicker foils
- (ii) grafting rate is higher in high density polyethylene compared to low density polyethylene
- (iii) swelling rate of polyethylene by styrene is higher than the rate of grafting

we have shown in a previous paper⁶ that at the given experimental conditions, for 0.1 mm thick polyethylene foils, the propagation reaction is not controlled by diffusion of styrene into polyethylene foil.

The instantaneous rate of polymerization measured by calorimetry gives the possibility to obtain fine structure of kinetic curves. As can be seen in Figure 2 in the case of low density polyethylene the rate of polymerization decreases in reality slowly in time reaching a minimum and then increases again. There could be two reasons for decreasing of polymerization rate with time:

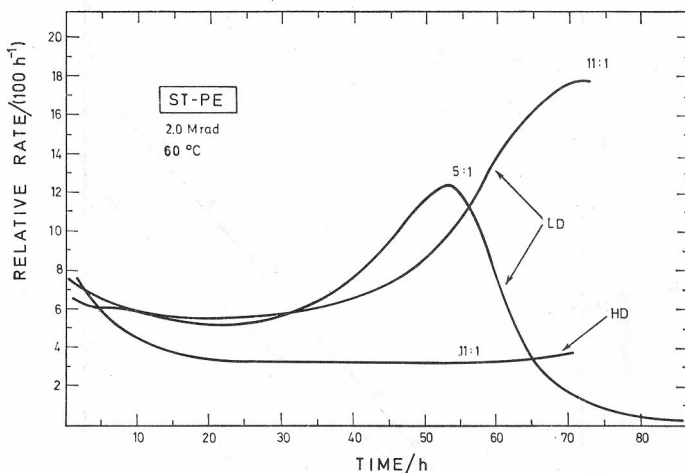


Figure 2. Dependence of graft polymerization rate on type of polyethylene and weight ratio styrene — polyethylene.

- (i) concentration of active centers decreases
- (ii) 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 is not possible to distinguish which of the two effects dominates.

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 foils 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. in most cases in grafting reactions termination reaction is diffusion-controlled.

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:

- (i) peroxy radicals reacting at the beginning
- (ii) peroxides decomposing slowly in the course of reaction.

Accordingly, in low density polyethylene the concentration of peroxides is much higher and they have dominating role in initiation process.

Methylmethacrylate-Polyethylene

In Figure 3 kinetic curves for graft copolymerization of methylmethacrylate at 60 °C onto low density polyethylene are shown. It is known that thermal polymerization of methylmethacrylate at 60 °C is negligible, and that gel effect is very pronounced in the polymerization of this monomer. In ad-

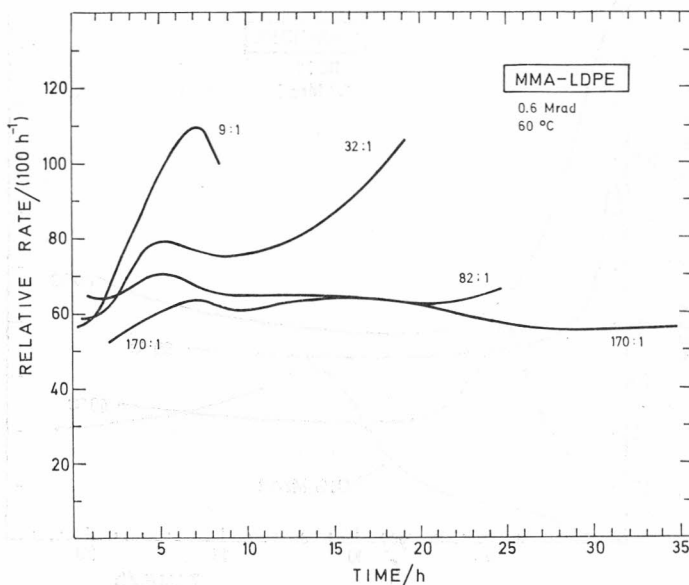


Figure 3. Dependence of graft polymerization rate on weight ratio methylmethacrylate — low density polyethylene.

dition, methylmethacrylate grafts more rapidly than styrene and the effect of monomer to polymer ratio is more pronounced if the ratio is smaller than 100 : 1 and if preirradiation dose is higher. This effect could be caused by inhomogeneous and slower supply of monomer inside the foil with increasing quantity of polymer due to sticking of polyethylene foils in calorimetric reaction vessel which has a limited volume. Lower monomer content inside the foils means higher viscosity which causes lower termination rate and therefore overall grafting rate is higher.

The fact that the grafting rate is lower at the beginning and increases until constant rate is established could be explained as follows:

Before the reaction starts polyethylene is swollen with methylmethacrylate, i. e. there is equilibrium with constant amount of monomer inside the foil. When the reaction begins the grafting rate is somewhat higher than the swelling rate. The monomer concentration inside the foil decreases leading to the increase of the viscosity of the medium; therefore the termination decreases and the grafting rate increases. With the increase of grafting yield the rate of swelling increases, too, and seems to become equal with grafting rate at about 300% grafting yield. The monomer concentration in foil becomes constant and grafting rate is constant until exhaustion of monomer in the reaction vessel. If the rate of initiation is higher, the effect is more pronounced as we observed if preirradiation dose was higher.

In Figure 4 kinetic curves for graft copolymerization of methylmethacrylate in the presence of high density polyethylene at 40 °C, 60 °C and 80 °C are

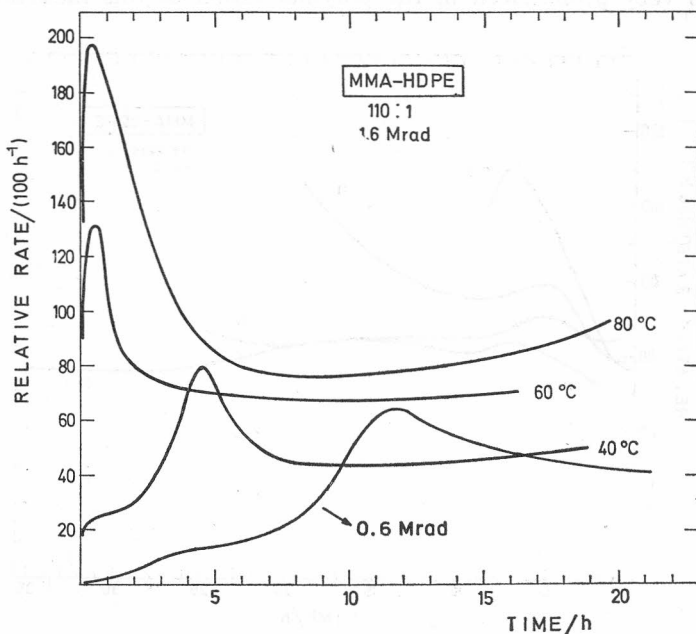


Figure 4. Dependence of graft polymerization rate of methylmethacrylate on high density polyethylene on temperature and preirradiation dose.

shown. 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.

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.

In Figure 5 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 are shown. It can be seen that after one week storage at room temperature the concentration of radicals is still high in polyethylene foils which results in higher polymerization rate at the beginning of reaction. Concentration of radicals decreases as storage time increases and after 11 weeks of storage practically all radicals have decayed. When graft copolymerization is performed at 40 °C (Figure 6) structural factors determine the rate of reaction at the beginning, their influence being higher as the concentration of active centers decreases with storage.

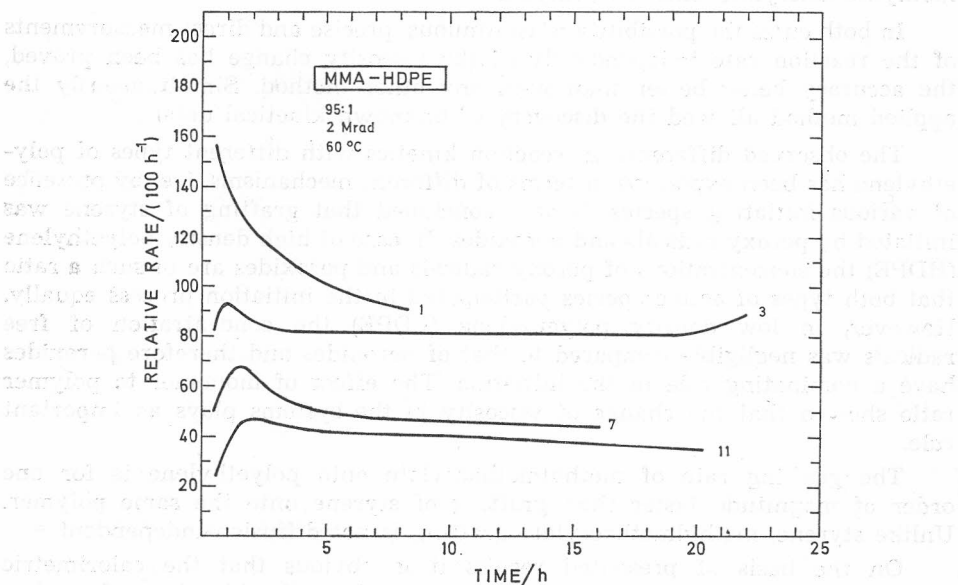


Figure 5. Dependence of graft polymerization rate at 60 °C on storage time of preirradiated polyethylene (1, 3, 7 and 11 weeks).

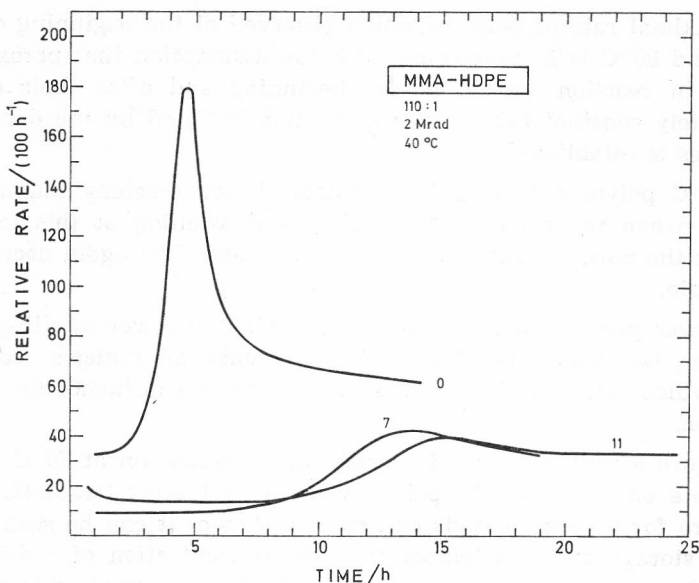


Figure 6. Dependence of graft polymerization rate at 40 °C on storage time of preirradiated polyethylene (0, 7 and 11 weeks).

CONCLUSION

Calvet microcalorimeter was used to follow the course of polymerization in a heterogeneous medium, i. e. radiation induced grafting of styrene and methylmethacrylate onto polyethylene.

In both cases the possibility of continuous, precise and direct measurements of the reaction rate independently of the viscosity change has been proved, the accuracy being better than with any other method. Simultaneously the applied method allowed the discovery of unknown kinetical details.

The observed difference in reaction kinetics with different types of polyethylene has been explained in terms of different mechanisms, i. e. by presence of various initiating species. It was concluded that grafting of styrene was initiated by peroxy radicals and peroxides. In case of high density polyethylene (HDPE) the concentrations of peroxy radicals and peroxides are in such a ratio that both types of active species participated in the initiation process equally. However, in low density polyethylene (LDPE) the concentration of free radicals was negligible compared to that of peroxides and therefore peroxides have a dominating role in the initiation. The effect of monomer to polymer ratio showed that the change of viscosity in the systems plays an important role.

The grafting rate of methylmethacrylate onto polyethylene is for one order of magnitude faster than grafting of styrene onto the same polymer. Unlike styrene, methylmethacrylate grafting is not diffusion-independent.

On the basis of presented results it is obvious that the calorimetric method reveals new and valuable information about the kinetics and mechanism of polymerization in heterogeneous mediums, which cannot be obtained

by another method. We refer especially to the possibility of measuring the reaction kinetics up to extremely high conversions. The decay of active species (formed by preirradiation of polymer) in time can be followed by this method as well.

REFERENCES

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.
2. R. J. Ceresa (Ed.), *Block and Graft Copolymerization*, Interscience, New York, 1976.
3. J. Dobo, A. Somogyi, and T. Czvikovszky, *J. Polymer Sci. Part C* 4 (1964) 1173.
4. M. Barić, *Microcalorimetric Investigation of Polymerization Processes*, Ph. D. Thesis, University of Zagreb, 1975.
5. M. Barić, F. Ranogajec, and I. Dvornik, *Croat. Chem. Acta* 53 (1979) 61.
6. F. Ranogajec, I. Dvornik, and J. Dobo, *European Polym. J.* 6 (1970) 1169.

SAŽETAK

Kalorimetrijsko ispitivanje cijepjenja stirena i metilmetakrilata na polietilen prethodno ozračen na zraku

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Osnovni nedostaci postojećih i najčešće primjenjivanih metoda za mjerenje brzine polimerizacionih procesa su indirektno mjerenje, nedovoljna točnost i ograničena primjenljivost. Osobito je to naglašeno kod ispitivanja reakcija cijepjenja, gdje reproducibilnost nije velika, jer na točnost mjerenja mogu utjecati čak i različita svojstva pojedinih uzoraka polimera.

U ovom radu predložena je kalorimetrija, kao nova metoda bez navedenih nedostataka za ispitivanje polimerizacionih procesa i primijenjena za istraživanje radijacionog cijepjenja stirena i metilmetakrilata na polietilen.

Rezultati su pokazali da se kalorimetrijski brzina cijepjenja može mjeriti kontinuirano i neposredno u cijeloj oblasti konverzija s točnošću mnogo boljom nego s bilo kojom do sada upotrebljavanom metodom.

Zaključeno je da cijepjenje stirena nije kontrolirano difuzijom, što nije slučaj kod cijepjenja metilmetakrilata. Za oba monomera kinetika reakcije zavisi o tipu polietilena, što je posljedica različitih mehanizama, tj. u reakciji inicijacije učestvuju dvije različite čestice, peroksi-radikali i peroksidi. Njihova koncentracija je različita u dva tipa upotrebljenog polietilena. U polietilenu visoke gustoće obje aktivne čestice učestvuju podjednako u procesu inicijacije. U polietilenu niske gustoće koncentracija peroksi-radikala je zanemarljiva u usporedbi s koncentracijom peroksida, koji prema tome imaju odlučujuću ulogu u inicijaciji cijepjenja. Promjena viskoziteta medija po hodu reakcije i struktura polimera u slučaju polietilena visoke gustoće utječu na kinetiku reakcije cijepjenja.

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