

The Simple Preparative Synthesis of Graft Copolymers of Polyethylene-Acrylamide

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Summary

The synthesis of polyethylene-g-acrylamide system was carried out at 40°. It was found that the graft of acrylamide is a linear function of the monomer's concentration, the duration of the reaction and has extremal character toward the initiators content (Fe^{2+} , hydroquinon - Na_2SO_3). The hydrophilic gel immobilised onto polyethylene surface can be formed by this way.

Introduction

Radiation technic is widely used for preparation of graft copolymers. Grafting of acrylamide onto polyolephines surface was studied in detail for instance by BATTARD, TREGGAR 1967, ROSENBLUM et al 1966. Usually these reactions are carried out at elevated temperatures (70 - 90°). However in some cases one needs to synthesize such copolymers in mild condition and moderate temperatures.

The present work deals with search of optimal conditions for synthesizing of graft copolymers polyethylene-

acrylamide at the temperature not higher than 40°.

Experiment

Film made from nonstabilized low density polyethylene was used for grafting following by post-effect technics.

Initial monomers: acrylamide, N,N'-methylenebisacrylamide ("Reanal" Hungary).

Co⁶⁰-source, 300,000 curie, was used for irradiation; dose capacity 0.1 - 1 Mrad/h, integral dose 1 - 20 Mrad. Films were thoroughly washed by water, acetone, ether and irradiated in air. Irradiated samples were put into glass ampules connected with vacuum line and flask contained monomer solutions (5 - 25 % acrylamide, 0 - 5 % N,N'-Methylenebisacrylamide) in water-alcohol (0 - 100 % i-PROH) and Fe²⁺ salt (10^{-5} - 10^{-2} g-ion/l) or mixture of hydroquinone - Na₂SO₃ (10^{-5} : 10^{-5} - 10^{-2} : 10^{-2} mole/l).

After evacuation the flask content was subjected to contact with irradiated polyethylene film and kept at fixed temperature. Resulting samples were washed off the initial reagents and homopolyacrylamide by water for 4 hours.

IR-spectra were registered using Perkin-Elmer-599 apparatus.

Results and Discussion

Preirradiated polyethylene (0,1-0,2 Mrad/h, 5-20 Mrad) has been found to induce the effective poly-

risation of acrylamide resulting in the formation of graft copolymers. Further on films which got a dose up to 10 Mrad with dose capacity 0,2 Mrad/h were used. The formation of graft copolymers was proved by IR -spectra of product (appearance of the absorption band at 1650 cm^{-1} corresponding to C=O oscillations in amide group, fig.1), and by weight control.

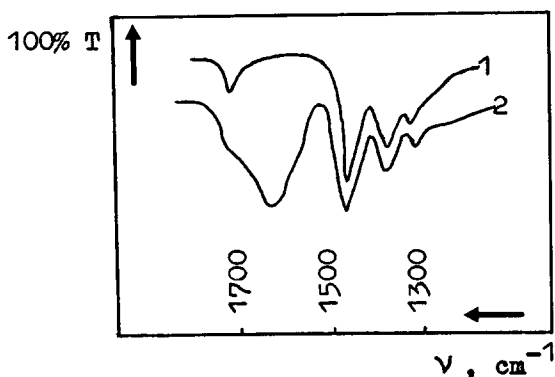


Fig.1

IR-spectra: 1-polyethylene, 2-polyethylene with grafted acrylamide.

As it is known the redox systems diminish to a great extent the initial polymerisation temperature and inhibit homopolymerisation (BATTARD, TREGGAR, 1967, DOLGOPLASK, TINYAKOVA, 1972). We have studied the influence of Fe^{2+} concentrations or mixture of hydroquinone and Na_2SO_3 on the acrylamide graft copolymerization to polyethylene.

It was found that presence of Fe^{2+} ions decrease

the initial polymerization temperature in such a way that even at 20° graft copolymerization becomes possible (fig.2). The homopolymerization of acrylamide is changed significantly also in dependence of Fe^{2+} concentration. At the content of Fe^{2+} less than 10^{-5} g-ion/l the highly viscous gel is formed. At higher content of Fe^{2+} the gel's viscosity is going down and at Fe^{2+} content 10^{-3} g-ion/l gel formation does not take place at all. It should be noted that the degree

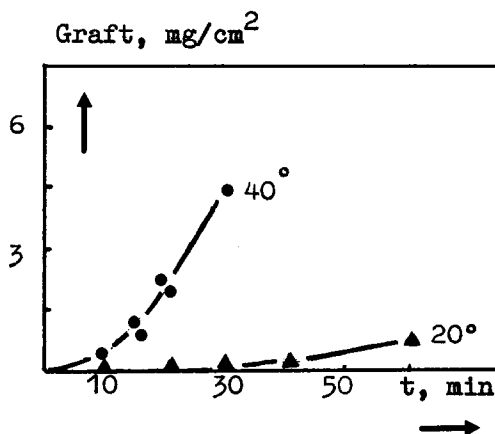


Fig.2

The influence of polymerization time on grafting of acrylamide (Fe^{2+} 10^{-3} g-ion/l, 0,1% N,N'-methylenebisacrylamide, 10% i-PrOH)

of grafting is also changed at the same time (fig.3). Similar changes are observed when the mixture of hydroquinone - Na_2SO_3 is used.

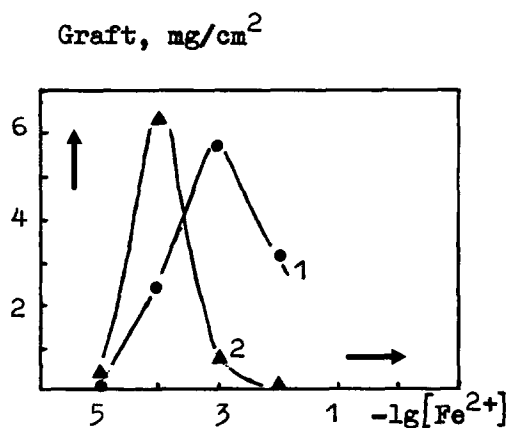


Fig. 3

The influence of Fe^{2+} concentration - 1 (40°, 30 min, 15% acrylamide) and hydroquinon - Na_2SO_3 concentration - 2 (40°, 60 min, 15% acrylamide) onto grafting of acrylamide.

It may be assumed that such change in grafting as a function of Fe^{2+} content is connected with difficulties of monomer diffusion to polyethylene surface at low concentrations as highly viscous gel is formed and the degree of grafting is going down. The fast degradation of hydroperoxide groups on polyethylene surface and recombination of radicals when Fe^{2+} concentration is more than 10^{-3} g-ion/l takes place which results in inhibition of grafting.

Time and monomer concentration dependences are shown on Fig. 2 and Fig. 4. As it is seen from these figures the amount of grafted monomer is increased almost linearly with the increase of both parameters,

this is in agreement with data in literature (ROZEN-BLUM et al 1966).

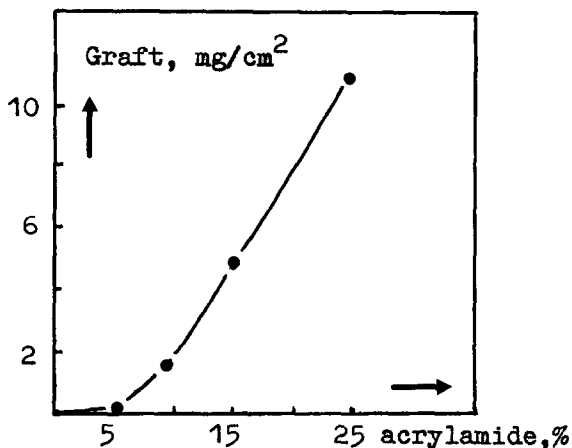


Fig.4

The influence of acrylamide concentration (reaction time 2.5 hours) on grafting (Fe^{2+} 10^{-3} g-ion/l, 0.1% N,N'-methylenebisacrylamide, 10% i-PrOH)

So the optimal conditions for synthesis of graft-copolymers polyethylene-acrylamide at 40° were found to be : 15% acrylamide H_2O -i-PrOH solution (10% i-PrOH), 0.1% N,N'-methylenebisacrylamide solution and 10^{-3} g-ion/l solution Fe^{2+} . The hydrophilic gel immobilized onto polyethylene surface can be formed by this way.

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