

CATIONIC MODIFICATIONS OF POLYALKENES II. EFFECT OF A SINGLE OR CONTINUOUS SUPPLY OF Co-INITIATOR*

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For an effective modification of polyalkenes leading to the formation of block and/or graft copolymers, the presence of co-initiating water is absolutely necessary. We have compared two procedures used in the co-initiation of cationic reactions on polymers. Gradually supplied air moisture raises the efficiency of modification of isotactic polypropylene with poly(oxyethylene) several times, compared with a single addition of co-initiating water.

By contacting superacids and polyalkene chains, carbocations can be generated at the ends and/or internal units of macromolecules¹. Under suitable conditions, such cationic sites can initiate formation of chains from cationically polymerizing monomers or react directly with a heteroatom² or a polar group³⁻⁵ of other polymers, giving rise to block and/or graft copolymers. The properties of polyalkenes can be modified in a wide range by employing the suggested procedure.

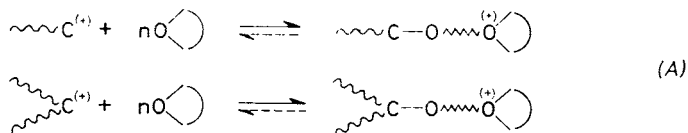
The formation of polypropylene (polyethylene) copolymers with polyethers and/or poly(dimethylsiloxane) can schematically be described by reactions (A) or (B), in which



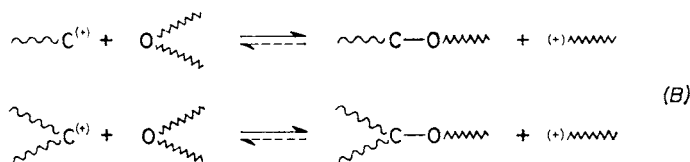
denotes the polyalkene chain,



denotes the chain of the modifying polyether (e.g., poly(oxyethylene)), poly-(dimethylsiloxane); $\text{O} \langle \rangle$ symbolizes the oxygen-containing heterocycle, e.g., tetrahydrofuran (counter-ions have been omitted for the sake of simplicity).

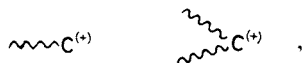


* First part: Collect. Czech. Chem. Commun. 54, 109 (1989).



One of the conditions necessary for the formation of copolymers by routes indicated above is the presence of a co-initiator, e.g., water.

Co-initiating water may affect the formation of carbocations



exchange reactions (B), and it also markedly retards the polymerization of tetrahydrofuran (A)⁶. The dependence of the copolymer yield on the concentration of the co-initiator has a sharp maximum². It is not without importance, therefore, in which stage of the process does water enter the system, at what concentration and in what way it is distributed to the sites. Local excess of the co-initiator in the cases of its single supply deactivates carbocations in the respective space. Only the remaining carbocations, reached by just the necessary number of molecules of the activating component, can be used in the modification reactions. Under otherwise identical conditions, the amount of modifying polymers bound on polyalkene chains should depend on the procedure of dosage of the co-initiator. We tried to verify this assumption by comparing the effects of a single and a continuous supply of water into the reaction space.

EXPERIMENTAL

Materials

Isotactic polypropylene (unstabilized, M_n 76 400) and polyethylene (LITEN, M_n 23 000) were commercial batches (CHZ ČSSP, Litvínov, Czechoslovakia). Poly(oxyethylene), M_n 6 000 (CHZWP, Nováky, Czechoslovakia), was dissolved in tetrahydrofuran (THF), the solution was purified and dried with sodium metal, filtered and used either directly, or poly(oxyethylene) was isolated from it by evaporation of tetrahydrofuran in high vacuum. The chemicals have been characterized earlier^{2,5}.

Modification Reactions

Into a glass reactor (Fig. 1) of a high-vacuum line, 1.5 g polypropylene or polyethylene was introduced through opening 4, which after that was sealed, or a closed capillary 8 was sealed to it. After the system was fixed to the line by sealing in point 2, the polymer was dried with stirring by means of a magnet at $\sim 10^{-3}$ Pa, and 5 cm³ of the wetting agent was distilled (for reactions (A) tetrahydrofuran, for reactions (B) tetrahydrofuran or benzene). Vacuum was then removed by pure dry nitrogen (below, only nitrogen; containing less than 1 ppm O₂ and H₂O)

supplied through the joint with the line, at a pressure of c. 10^5 Pa. The siloxonium dication (DIC)⁷ dissolved in benzene, and co-initiator (if used) (in THF, or in benzene solution⁸) were dosed with an injection syringe against a stream of nitrogen after the tip of tube 1 had been cut off. The open end of the tube was then immediately sealed, the suspension was stirred, the solvent removed by distillation in vacuum, the reactor was sealed off from the line in point 3 and placed in a thermostat (at T_i). After a chosen time of interaction t_i the apparatus was again fixed to the line by sealing an extension piece 7, the inner space of the piece was dried, the break seal 6 was broken, and the middle stage of the operation proceeded by one of the procedures described below:

a) On cooling the inner part of the reactor with liquid nitrogen tetrahydrofuran was distilled; in experiments with a single supply of the co-initiator the reactor was thermostated, the vacuum was removed by nitrogen, the tip of tube 1 was cut off, and the solution of the co-initiator was dosed against a stream of nitrogen.

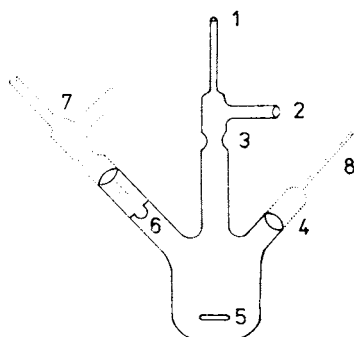
b) The vacuum was removed with nitrogen, the tip of tube 1 was cut off, and a solution of the modifying polymer (sometimes, with co-initiator) prepared in a similar apparatus on the line (with exclusion of contamination) was introduced against the stream of nitrogen by means of a syringe needle.

This was followed (in each case) by separating the apparatus from the line by blowing off at the point 7, and the apparatus was then placed in a thermostat (for t_m at T_m). Gradual supply of co-initiating water was made possible by breaking off the tip of capillary 8 of the apparatus thermostated immediately before. After completed modification, the reactor was cut into pieces, its contents were introduced into methanol (200 cm^3) and decanted with methanol at least three times.

Separation of copolymers from homopolymers by multiple extractions was carried out in cylindrical thermostated vessels, in which the modification product (1.5–13 g) was stirred with 60 cm^3 of the solvent of the modifying component for 8 h, after which the solid and liquid phases were separated (by sedimentation or centrifugation), the solid phase was returned into the extractor and extract again. The pure liquid phases were evaporated to dryness and the procedure was repeated, until the mass of the dry residue became lower than 2 mg. The polyalkene content in soluble fractions was measured with an NMR spectrophotometer Tesla BS 567 A at the working frequency 100 MHz and intensity of the magnetic field 2.35 T. Composition of some insoluble fractions after solvent extraction was determined by the absorption spectroscopy of films with a UR-10, Zeiss, Jena apparatus.

FIG. 1

Reactor for the modification of polyalkenes: 1 tube for the dosage of initiators, co-initiators and solutions of modifying polymers; 2 attachment to the high-vacuum line; 3 construction for sealing off; 4 feed hopper; 5 stirrer; 6 break seal; 7 feed hopper with stirrer allowing reattachment to the high-vacuum line; 8 capillary for gradually penetrating air moisture



RESULTS AND DISCUSSION

By the procedure used in supplying co-initiating water, in fact by a slow contamination of the reaction medium with air moisture diffusing through a long and narrow capillary, the amount of poly(oxyethylene) bonded to the polypropylene matrix was raised considerably. Quantitative data on the effectiveness of modifications and their reliability depend on the precision of separation of copolymers from homopolymers. None of the methods known so far ensures a clear-cut separation of these types of macromolecules. The best results can be obtained by extracting mixtures of components possessing diametrically different solubilities, e.g. of isotactic polypropylene and poly(oxyethylene) or poly(oxytetramethylene) and their copolymers. An example of separation of a mixture of such macromolecules by multiple extractions is given in Fig. 2.

Water dissolves poly(oxyethylene) and low-molecular weight poly(oxytetramethylene), 2-propanol, the residue of poly(oxytetramethylene) and chains of polypropylene copolymers with a large number of polyether grafts. The limit of solubility depends of course on the molecular weight of the hydrocarbon and modifying chain. Polypropylene sequences occur in soluble fractions into which they cannot penetrate in the homopolymer form. On the other hand, evidence which proves the existence of the modifying polymer in the extracted insoluble fraction proves at the same time the existence of the copolymer in this fraction, because the modifying homopolymer would be extracted. The difference in the weight of polyalkene used in the modification and in the weight of the extracted insoluble fraction is also a preliminary criterion. This difference proves the formation of copolymers. Zero difference proves nothing, however, since compensation may occur in this case. These findings reduce the accuracy of determination of the efficiency of modifications, in many cases to a mere statement whether the copolymer is formed or not.

The effect of the procedure used in the supply of co-initiating water to the carbocationic sites on the effectiveness of isotactic polypropylene (*i*-PP) grafting with polyethers and poly(dimethylsiloxane) (PD) is described by the results summarized in Table I.

Grafting of the isotactic polypropylene matrix with the tetrahydrofuran monomer (reaction A – grafting form) is not affected to any important degree by the procedure of water dosage, if the latter is added only after a sufficiently long time of interaction of the dication with polypropylene. While water added in a single supply is gradually removed from the reaction medium by transfer reactions and ceases to retard the polymerization of tetrahydrofuran, gradual supply of water distinctly reduces the weight of polytetrahydrofuran in the product (cf. Y in the first two lines and the procedure used in dosing C and D in Table I).

Only a small amount of the solvent – tetrahydrofuran – polymerizes in the modification with poly(oxyethylene) (POE). In a system with water added in a single

TABLE I

Effect of the dosage of co-initiating water on the effectiveness of isotactic polypropylene modification (C single supply, $H_2O : DIC = 0.5 : 1$ mol; D gradual; C, D only after interaction between DIC and polypropylene, E single supply along with DIC). Symbols: Y is the total yield, G is the insoluble fraction, C_G is the fraction of the modifying component in the insoluble fraction, C_S is the fraction of polypropylene in the solid phase from the first extract. Conditions: 1.5 g *i*-PP, 0.09 mmol DIC, t_i 1–2 days, T_i 295 K (cf. text); 20 cm³ THF or 1 g POE in 15 ml THF or 1 g PD in 10 ml benzene, t_m 7 days, T_m 295 K (cf. text)

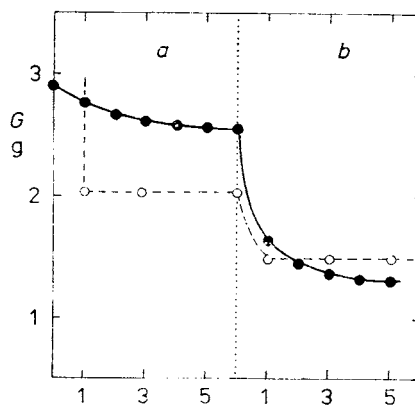
Dosage of water	Modifying component	Y g	G g	C_G wt %	C_S mole %	Extraction agent
C	THF	9.9	1.38	— ^a	29	2-propanol
	THF ^b	13.1	1.46	4.8 ^c	37	2-propanol
	POE	2.9	1.36	3.0 ^c	—	2-propanol
	PD	1.7	1.48	— ^a	62	benzene
D	THF	5.7	1.51	— ^a	—	2-propanol
	THF ^b	5.1	1.45	— ^a	—	2-propanol
	POE	2.5	2.21	31.9	—	2-propanol
	PD	1.7	1.48	— ^a	7	benzene
	PD ^d	2.3	1.32	— ^a	2	benzene
E	THF ^e	2.9	1.48	0	0	2-propanol

^a The amount of bound modifying polymer could not be determined from the weight balance.

^b T_i 263 K. ^c Analysis by IR spectroscopy. ^d 0.01 mmol DIC. ^e 5 cm³ THF along with H₂O and DIC.

FIG. 2

Multiple extraction of the modification product of isotactic polypropylene with poly(oxyethylene) in tetrahydrofuran (cf. Table I, C, line POE). G insoluble fraction in extraction; e number of extractions (each extraction lasted 8 h); a extracted with water at 298 K; b extracted with 2-propanol at 333 K; ----- extraction of mixtures of homopolymers (1 : 1 : 1) without copolymer component



supply only a few weight per cent of poly(oxyethylene) are bound to polypropylene. By using a capillary having a suitable bore and length, the rate of air moisture supply to the active sites can be regulated, and the latter can be activated for exchange reactions with poly(oxyethylene) much more effectively. Under otherwise identical conditions, the amount of the copolymer increases by an order of magnitude. The presence of water in the interaction of the dication with polypropylene in the presence of tetrahydrofuran does not stimulate the formation of copolymers (cf. E in Table I).

The amount of copolymers formed in reactions with atactic polypropylene is higher several times than in the grafting of isotactic polypropylene. Modification of polypropylene oil (containing multiple bonds) is even more effective. Atactic polypropylene has a relatively low molecular weight and is partly soluble in 2-propanol (~70%). Atactic polypropylene modified with poly(oxyethylene) is completely soluble in 2-propanol. The modification product dissolves in water by some 50%, and the two components, i.e. atactic polypropylene and poly(oxyethylene), were detected in both fractions. The modification product of polypropylene oil with poly(oxyethylene) is completely soluble in water. Numeric data regarding the polypropylene to poly(oxyethylene) ratio are subjected to a large error and are therefore omitted.

The modification process of isotactic polypropylene with siloxanes is marked by their reactions. The degradation of poly(dimethylsiloxane) chains with superacids leads to a considerable decrease in the molecular weight of the polymer, to a decrease in the length of blocks and/or grafts in the copolymer, and thus also in the weight of the modifying component. Co-initiation with gradually supplied water allows lower concentrations of the dication to be used, and the weight of bound poly(dimethylsiloxane) increases. Copolymer with a high content of the siloxane component dissolves in benzene.

The possibility of formation of copolymers of linear polyethylene with poly(oxyethylene) is lower by as much as an order of magnitude, compared with isotactic polypropylene. Only ~2% of the modifying component were detected in the modification products. It has been confirmed that in the absence of tertiary carbon atoms in polyalkene chains carbocations are not formed on macromolecules of the polymer in a sufficient amount².

SbCl₅ was also used in the generation of cationic active sites. The formation of the copolymer of polypropylene with poly(oxyethylene) showed (by means of NMR) that polyalkene was present in fractions soluble in the extraction with 2-propanol, in quantities amounting to a few per cent.

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