



and a certain amount of coinitiator we succeeded to create a sufficient number of cationic active centres (AC) on polyalkene chains. This enabled subsequent modification reactions: (i) with monomers which can be polymerized cationically (e.g. cyclic ethers as tetrahydrofuran (THF), "grafting from"); (ii) with polymers containing O heteroatoms (poly(oxyethylene), poly(oxytetramethylene), poly(oxy-2,6-dimethyl-1,4-phenylene), poly(dimethylsiloxane)).

## EXPERIMENTAL

The experiments were carried out in glass reaction vessels (Fig. 1) attached to a vacuum line. The vessels were dried in vacuo of  $10^{-2}$ – $10^{-4}$  Pa. The initiator, coinitiator and solutions of modifying components were introduced into the reaction vessels using hypodermic syringe and dry, oxygen-free nitrogen cushion. The effectiveness of water-removal from solvents was checked by means of radical ions.

Polyalkene (1.5 g) with particle diameter  $< 90 \mu\text{m}$  was pumped out in the reactor at  $< 10^{-2}$  Pa 6 h. Then 5 ml benzene was distilled-in, 0.09 mmole dication in benzene was introduced (against nitrogen stream), the mixture homogenized and benzene pumped out.

The interaction of polyalkene with dication (temperature  $T_i$ , time  $t_i$ ) led to formation of carbocations on the hydrocarbon macromolecules. To the latter system, a solution of the modifying polymer [i.e. poly(oxyethylene) or poly(oxytetramethylene) or poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(dimethylsiloxane)] (1 g) or monomeric THF or — in case of modification by siloxanes — octamethylcyclotetrasiloxane (20 ml) and coinitiator ( $\text{H}_2\text{O}$ ) were added. Modification was carried out at temperature  $T_m$  for a certain period of time ( $t_m$ ). The product containing (theoretically) macromolecules of both matrix and modifying polymers and a copolymer (block and graft) was precipitated by an excess of methanol.

The dry products were carefully extracted with suitable solvents dissolving the modifying component. The extractions (described in detail in a preceding paper<sup>3</sup>) were repeated as long as the mass of extracted material after drying was not greater than 2 mg. Typically 10–20 extrac-

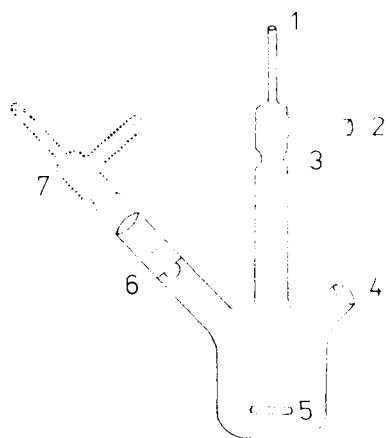


FIG. 1

Reaction vessel for modification reactions: 1 inlet tube for dosing initiators, coinitiators or solutions of modifying polymers, 2 vacuum line attachments, 3 seal-off point, 4 inlet port, 5 stirrer, 6 bubble break seal, 7 attachment with stirrer enabling repeated sealing to vacuum line

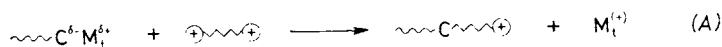
tions were necessary. As the copolymer is also partially dissolved during extractions its formation could be demonstrated by measuring NMR and IR spectra of soluble as well as insoluble fractions.

The changes of polypropylene molecular mass by the action of dication were measured as follows: polypropylene (1.5 g) with  $\bar{M}_v$  289 000 was treated with 0.023–0.25 mmole of siloxonium dication at room temperature ( $t_1$  7 days) in the presence or absence of the cointitiating water. The product of this treatment was precipitated and washed by methanol and its  $\bar{M}_v$  redetermined, obtaining values 275 000–290 000.

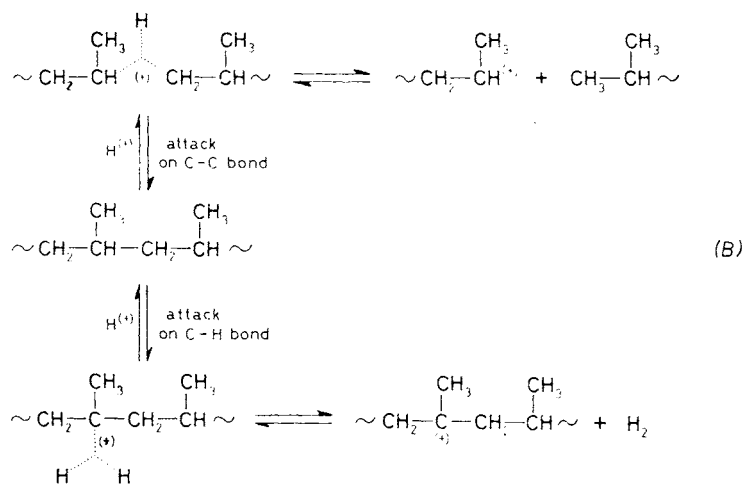
Composites of isotactic polypropylene with calcium carbonate were prepared by mixing the components in a Platicorder Brabender laboratory mixer (60 g, 403 K, 10 min). The test specimens were made out of the resulting material by pressing. Standard testing procedures were applied to measure some physico-mechanical properties.

## RESULTS AND DISCUSSION

One of the possible reaction sites likely to form a cationic active centre is the carbon–metal bond from the ZIEGLER-NATTA polymerization centre. The excess of electrons on this carbon atom offers the possibility of its combining with a dication



Other centres liable to cationic attack are various defects on polyalkene chains (multiple bonds or carbonyls formed through oxidation). Cationic centres may also be created by C–C and C–H bond scissions of polypropylene chains:



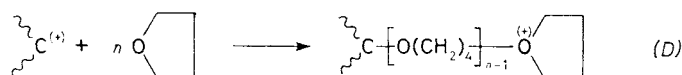
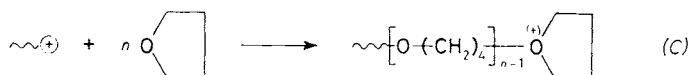
Polyethylene<sup>4</sup> and other polyalkenes exhibit similar reactions. Another strongly acidic species, such as  $\sim\text{Si}^{(+)}$  (from siloxonium dication), may function instead

of proton  $H^{(+)}$ . Scheme (B) is thus modified accordingly. When comparing the modifying efficiency of polypropylene and polyethylene, resp., it was shown that the interaction of low-molecular dication or macrocation with polypropylene chain was most pronounced. A mixture of products containing a certain number of carbocations is formed by breaking C—H and C—C bonds during the interaction of siloxonium dication or other superacids with the polypropylene matrix. In order to distinguish which of these attacks is more important during cationic scission the viscosity molecular weight ( $M_v$ ) was measured in all cases after the interaction of polypropylene with various amounts of dication. As no crosslinking was observed and no significant changes of  $M_v$  were noted (only a slight decrease when increasing the initiator level), it was concluded that the active centre is most frequently formed through tertiary hydrogen abstraction from polypropylene main chain.

The rate of tetrahydrofuran polymerization on thus formed cationic active centres is greater than during the initiation by dication alone (the amount of poly(oxytetramethylene) formed on carbocations is by 10% greater than in the case of dication initiation).

The modification efficiency is strongly influenced by the amount of initiator, time and temperature of dication interaction with polypropylene, the amount of added co-initiating  $H_2O$ , and by the time and temperature of modification itself (i.e. the reaction of carbocation with tetrahydrofuran or polyether polymer chain or poly(dimethylsiloxane).

The influence of individual variables upon the result of modification was examined on the reaction of cationic active centres with tetrahydrofuran monomer ((C), (D)).



It is obvious that the copolymers of polypropylene with polyethers (poly(dimethylsiloxane)) are always present in the product if the insoluble part after the extraction with 2-propanol (benzene) at 333 K is greater than the mass of the initial polymer matrix (1.5 g). Part of copolymer with high poly(oxytetramethylene) (poly(dimethylsiloxane)) content is, however, transferred into soluble fractions. The amount of insoluble fractions reflects the quantity of bonded poly(oxytetramethylene), when expressed as a dependence on  $t_i$ ,  $T_i$ ,  $t_m$  and  $T_m$ , resp. and exhibits a flat, nonpronounced maximum for  $t_i$  1 day,  $T_i$  263 K,  $t_m$  7 days and  $T_m$  263–295 K.

The presence of coinitiating amount of water is a necessary condition to achieve an efficient modification by the siloxonium dication (Fig. 2). Water, when added in a single step and in a great amount retards and finally stops the polymerization of tetrahydrofuran. Small amounts (0.3–0.5 mmol/1 mmol (DIC)) are, however, essential to obtain the modified polypropylene. The maximum of bonded poly(oxytetramethylene) is very sharp.

When attempting to modify linear polyethylene it was not possible to attach more than several per cent of poly(oxytetramethylene) chains. The comparison of these results with those obtained with polypropylene matrix indicates the ability of tertiary hydrogens on polypropylene chains to form cationic active centres.

Another mode of synthesis of amphiphilic copolymers is based on exchange reactions with polar polyethers:

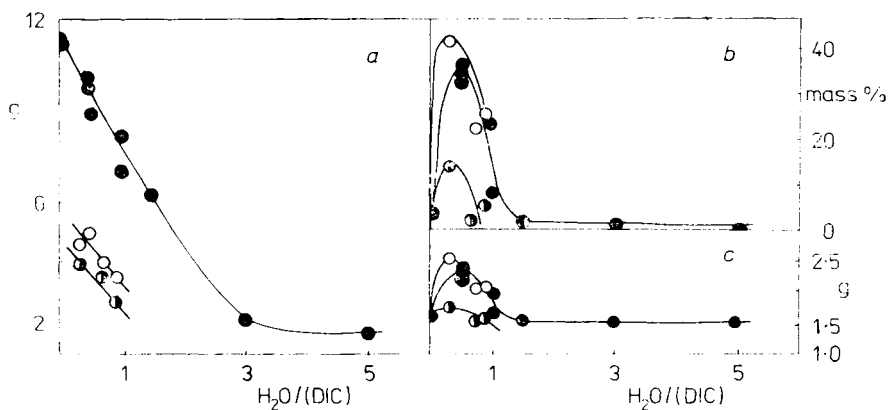


Fig. 2

The influence of coinitiating water upon the formation of copolymers polypropylene-*block*-poly(oxytetramethylene) and polypropylene-*graft*-poly(oxytetramethylene): *a* overall yield of modification (g), *b* amount of bonded poly(oxytetramethylene) (mass %), *c* insoluble parts in 2-propanol at 333 K (g). Modifying component 20 cm<sup>3</sup> THF. Curves (symbols in the scheme): ○ *t*<sub>i</sub> 1 day, *T*<sub>i</sub> 263 K, *t*<sub>m</sub> 9 days, *T*<sub>m</sub> 263 K; ● *t*<sub>i</sub> 2 days, *T*<sub>i</sub> 295 K, *t*<sub>m</sub> 9 days, *T*<sub>m</sub> 263 K; ● *t*<sub>i</sub> 2 days, *T*<sub>i</sub> 295 K, *t*<sub>m</sub> 4 days, *T*<sub>m</sub> 295 K

This mode may be further developed by its combination with the polymerization of cationically polymerizing monomers on carbocations (e.g. during the modification by poly(oxyethylene) dissolved in tetrahydrofuran). A part of copolymers may be formed also through bonding of polyether macrocations on polyalkene chains.

The efficiency of polypropylene modification by polymeric living poly(oxytetramethylene) (grafting onto) is lower than during the reaction on carbenium active centres utilizing monomeric tetrahydrofuran (grafting from). Poly(oxyethylene) dissolved in tetrahydrofuran gives the best results of modification by polyethers. In this case, only a small quantity of poly(oxytetramethylene) is formed (<50% in comparison with the modification without poly(oxyethylene)).

TABLE I

Comparison of properties of filled polypropylene (Mosten 55 212): A PP containing standard treated filler (40 mass %), micro-ground  $\text{CaCO}_3$  (Durcal 2); B PP containing non-treated Durcal 2 (40 mass %) and polymeric compatibilizing additive (2 mass %), polypropylene-*graft*-poly(oxyethylene)-*graft*-poly(oxytetramethylene) (40 : 60 (mass %), polypropylene : polyether)

Propert	A	B
Melt flow index 21N, $\text{g } 10^{-1} \text{ min}^{-1}$	0.66	1.13
Melt flow index 49N, $\text{g } 10^{-1} \text{ min}^{-1}$	2.97	5.09
Yield point, MPa	22.1	18.6
<i>E</i> -modulus, GPa	2.4	2.04
Elongation at break, %	460	488
Impact strength, $\text{kJ m}^{-2}$	200	245
Notched impact strength, $\text{kJ m}^{-2}$	5.6	7.6
Thermal stability due to Vicat, K	380	373

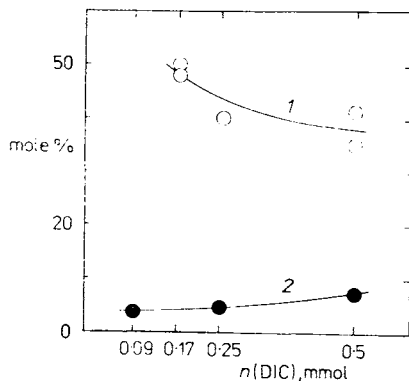


FIG. 3

Modification of *isotactic* polypropylene and linear polyethylene by poly(oxy-2,6-dimethyl-1,4-phenylene). Modifying component 1 g poly(oxy-2,6-dimethyl-1,4-phenylene) in  $15 \text{ cm}^3$  benzene. NMR determination of polyalkene content in first fraction after benzene extraction: 1 *isotactic* polypropylene,  $t_i$  1 day,  $T_i$  295 K, (DIC)/ $\text{H}_2\text{O}$  1 : 0.5,  $t_m$  12 days,  $T_m$  295 K; 2 linear polyethylene, the conditions as above (curve 1)

In order to prepare polyalkene copolymers with poly(oxy-2,6-dimethyl-1,4-phenylene) two possibilities may be employed: the reaction of cationic active centres either with polyether chain or with the aromatic ring. The extent of these two reaction modes was estimated by the crosslinking reaction of poly(oxy-2,6-dimethyl-1,4-phenylene) effected by the siloxonium dication. The amount of insoluble products varied according to the concentration of initiator (0.09–0.5 mmole (DIC)) and was found to lie within 1–6 mass %. This relatively small amount of cross-linked fractions clearly indicates that the copolymers are formed predominantly via ether bond scission and not through the reaction with aromatic ring. Long poly(oxy-2,6-dimethyl-1,4-phenylene) chains ( $\bar{M}_n \sim 50\,000$ ) carry even the grafted polyalkene molecules into the solution during the extraction. Fig. 3 shows the comparison modifying efficiency in the case of polypropylene (tens of mole % *isotactic* polypropylene) and polyethylene (mol % linear polyethylene) chains which were modified using poly(oxy-2,6-dimethyl-1,4-phenylene). The efficiency was established by determining the amount of polyalkenes in soluble part of product after the first extraction with benzene at 333 K.

The copolymers of polyalkenes with polysiloxanes are formed by the reaction of carbocations on the polyalkene chains with suitable siloxane monomers (octamethylcyclotetrasiloxane being predominantly applied) or directly, by the attack of this carbocations on oxygen atom of polysiloxane chain. After the hexane extraction of this reaction products at 333 K 5 mass % of poly(dimethylsiloxane) was found in insoluble fractions. About 14% of *isotactic* polypropylene was extracted to soluble fractions as copolymer.

A variety of composites prepared by using the compatibility-improving additives, synthesized via cationic reactions on polymers, may find a broad application range in practice. Compatibilizing activity of *isotactic* polypropylene terpolymer with poly(oxyethylene) and poly(oxytetramethylene) was demonstrated on *isotactic* polypropylene filled with non-treated micro-ground calcium carbonate (Durcal 2). The mechanical properties of this composite were compared with the similar composite filled also with 40% CaCO<sub>3</sub> which was, however, treated with 0.3% stearic acid and 0.5% calcium stearate (Table I).

Composite with copolymer exhibits higher toughness when compared with composites containing standard-treated CaCO<sub>3</sub>. At the same time the elongation and melt-flow index are increasing (the flow-in properties are improved). The decrease of stiffness-strength (*E*-modulus) and thermal resistance (Vicat) is substantially lower than one would expect judging from the decrease of yield point.

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