Selective Polymerization from Olefin Mixtures

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INTRODUCTION

For inorganic as well as for organic reactions the necessary raw materials in general are mixtures of different components. Different separation processes are needed before proceeding to the reactions resulting in the wished for transformation product. The development of new chemical procedures for obtaining energy or raw materials and their use without getting by-products or products without economical profit require new methods in chemical research.

One way is the reactive separation of one or two components from a raw material mixture. This method shows some advantages because separation methods need energy and time, with increasing expenditures for the production of intermediates or final products.

In the natural sciences one finds many examples where many elementary processes with high regio- or stereoselectivity take place from raw materials without pre-separation of the reacting components. Unfortunately, such processes in technical use are rare in consequence of the small volume-time ratio of such reactions.

During the last years this supposition, particularly for organic or metal-organic reactions, has been changed and the steering of the reactivity-selectivity-ratio remarkably improved. A deeper understanding of the nature of the elementary steps within chemical reactions and investigations of their quantitative description favors the development of a reaction theory [1]. In recent years new methods for multicomponent analysis have been created and several techniques for ultrafast spectroscopy or dielectric field relaxation methods have opened the way for modeling the course of the reaction and have

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shown the possibilities for variation of the properties of products
with technical application.

In polymer chemistry the successful work of Kennedy [2] on so-
called "ionic engineering" can be mentioned as one example.
Oligomerization or cyclooligomerization of butadiene, depending
on the Ni complex-triphenylphosphane ratio, might be another ex-
ample [3] of this trend. Manifold examples in this connection are
known from modern synthetic organic chemistry [4].

Besides various general reactions such as oxidation, hydrogenation,
addition, and complex formation, polymerization reactions might be
helpful for the reactive separation of olefins or diolefins which are
components, for example, of technical pyrolysis fractions. Selective
polymerization should have the additional advantage, compared with
the other reactions mentioned above, that it is easy to separate the
polymer products from the unreacting components.

1. SUPPOSITIONS FOR SELECTIVE POLYMERIZATION

The term "selective polymerization" was mentioned in the chemi-
cal literature more than 30 years ago and particularly refers to the
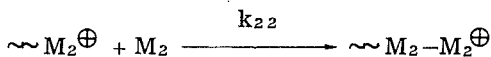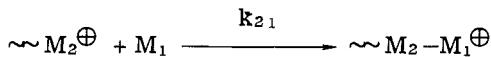dimerization of isobutene from a technical butene fraction [5].

Using industrial common Lewis acids (e.g., AlCl$_3$), the process
will not be selective either with reference to the formation of only
one dimer or relative to the only reaction of isobutene. Under these
conditions butene-1 will also react and different products are formed
by fast isomerization reactions via intermediary carbenium ions.
The formation of polymers from mixtures of polymerizable monomers
has never been stated except in the patent literature, and real evi-
dence for the polymerization of only one component from a mixture
is wanting.

According to Ref. 6, the formation of polybutadiene with 94% 1,4-
structure has been reported by direct polymerization from a tech-
nical C$_4$ fraction using cobalt naphthenate and diethylaluminum-
chloride as a catalyst. If isobutene is removed from a C$_4$ fraction,
the butadiene is polymerized from the remaining fraction with the
help of triisobutylaluminum and TiCl$_4$ [7]. The aspects of reaction
steering were shown in the investigations of Abed and Varadi [8]
where, by variations in the composition of the mixed initiator from a
C$_4$ fraction polybutadiene, copolymers and mixtures of different poly-
mers were obtained. The emulsion polymerization of butadiene from
a C$_4$ fraction by hydrated CoF$_2$ and RhCl$_3$ has also been reported
[9].

The formation of high molecular polyisobutene is normally per-
formed from pure isobutene. Low molecular weight products were
also obtained from butene fractions [10]. Vybihal [11] reported on
dimer and trimer formation in addition to the codimer of isobutene and
butene-1 when a butene fraction containing 40 mass-% of isobutene is

treated with a cation-exchange resin (sulfonated styrene-divinyl benzene copolymer). Polymerization reactions of isobutene from a butene fraction [12, 13] or of butene-1 by Ziegler-Natta catalysts [14] or copolymerization reactions by use of C_4 mixtures [15-17] have been claimed in the patent literature but without details on yields, selectivities, or structural data on the products.

In this paper the term "selective polymerization" means the only reaction of one component from a mixture of olefins or the binary copolymerization of two components of the mixture. From a kinetic view the term "selectivity" has several meanings which are different in their temporal reaction probabilities. The ratio of these probabilities depends on whether only one component polymerizes from a mixture of monomers or binary copolymerization takes place. On the basis of the "first-order model" for the propagation reaction or the crossed propagation reaction of the binary copolymerization [18-20], the following differences of velocity result:

$$\sim\!\!\sim M_1^{\oplus} + M_1 \xrightarrow{\quad k_{11} \quad} \sim\!\!\sim M_1\!-\!M_1^{\oplus}$$

$$\sim\!\!\sim M_1^{\oplus} + M_2 \xrightarrow{\quad k_{12} \quad} \sim\!\!\sim M_1\!-\!M_2^{\oplus}$$

$$\sim\!\!\sim M_2^{\oplus} + M_1 \xrightarrow{\quad k_{21} \quad} \sim\!\!\sim M_2\!-\!M_1^{\oplus}$$

$$\sim\!\!\sim M_2^{\oplus} + M_2 \xrightarrow{\quad k_{22} \quad} \sim\!\!\sim M_2\!-\!M_2^{\oplus}$$
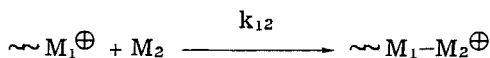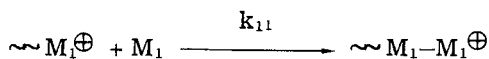
In principle, this equation system may be extended to more than two monomers $(M_1, M_2, ..., M_n)$, and for selectivity of the polymerization the findings can be paraphrased as follows [21]:

1. $(k_{21}, k_{11}) \gg (k_{12}, k_{22})$
   The polymerization of M_1 is dominant. This corresponds to real selective polymerization and we denote this case as "homoselective."
2. $(k_{11}, k_{22}) \gg (k_{12}, k_{21})$
   This corresponds to a mixture of two polymers, or under appropriate conditions (living chain ends) block copolymerization occurs. This case is denoted by "block-co-selective."
3. $(k_{21}, k_{12}) \gg (k_{11}, k_{22})$
   In this case, alternating copolymerization will be preferred. We denote it as "alternating-co-selective."
4. $(k_{11} \approx k_{12}); (k_{22} \approx k_{21})$
   Under these conditions one would expect random copolymerization, and the system is called "random-co-selective."

Besides the selectivity of the propagation reaction, for special reasons of reaction steering one can also reach a selective initiation of M_1 if there is a gradation within the relative reactivity of the monomers (e.g., isobutene and butene-1 with cationic initiators; $[k_i(M)_1 \neq k_i(M_2)]$). The same is true for selective chain termination or chain transfer reactions [2, 22].

With better information on the different reactivities of monomers and their growing abilities which affect the elementary steps by variation of the reaction conditions, a semiempirical reaction control for selective polymerization should, in principle, be possible. Favorable conditions can be paraphrased as follows:

1. The reactivities of monomers show remarkable differences due to initiators which prefer anionic, cationic, coordinative, or radical mechanisms.
2. Monomers which polymerize via the same mechanism show strong differences in their relative reactivities.
3. Initiation, propagation, or chain limiting reactions are influenced by "external parameters" which are not structure conditioned. This means the variation of the concentration ratio of the reactants, the variation of initiators or coinitiators, the influence of the relative reactivity by addition of donors or acceptors, the influence of solvents, the temperature, homogeneity or heterogeneity of the reaction system, and its temporal change.

Items 2 and 3 particularly favor ionic and coordinative reaction mechanisms for selective polymerization.

For a better understanding of selective polymerization, some general advantages of ionic polymerizations should be emphasized:

1. Some monomers are only (vinyl monomers with high π-donor capacity; e.g., isobutene) or primarily (e.g., obtaining special microstructures in the case of diene polymerizations) polymerizable via ionic mechanism.
2. At suitable reaction conditions via ionic or coordinative mechanisms, the formation of stereoregulated polymers is possible whereas this does not occur with the less selective radical chain formation reaction.
3. For special application fields of polymers (e.g., microelectronics, optics, polymeric drugs) the molecular weight distribution should be rather narrow. This might be realized by ionic mechanisms but is less probable by radical reactions.
4. Cyclic mono- and diolefins contained in pyrolysis fractions react in most cases of ionic polymerization via exocyclic double bonds whereas the endocyclic double bonds remain unreacted. This supports subsequent processes, e.g., vulcanization or other analogous polymer reactions.
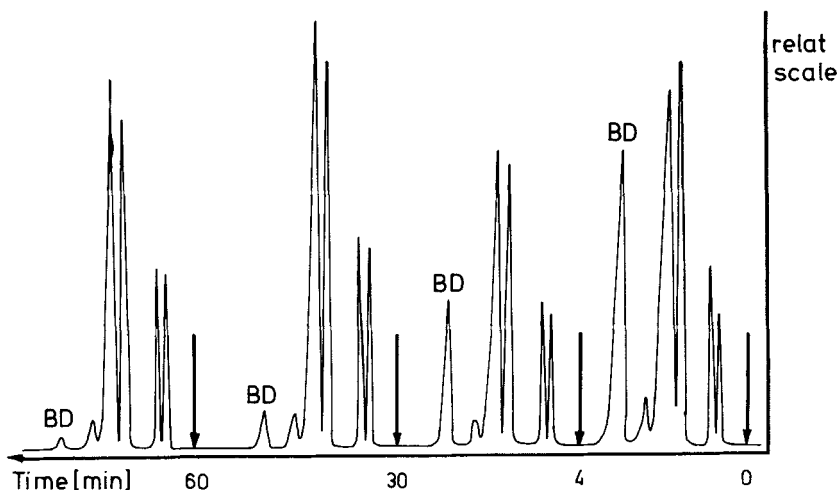
FIG. 1. Time-dependent selective polymerization of butadiene (BD) from a C_4 fraction by gas chromatography. Initiator: C_4H_9Li (7.5×10^{-3} mol/L). Solvent: THF. Temperature: 20°C.

5. The combination of different properties by co- and terpolymerization or grafting should be controlled much easier for ionic polymerization than for radical reactions.

Altogether it should not be overlooked that ionic polymerization needs a high level of technical effort, it should be used only when outstanding product qualities are needed which are not available by other methods.

2. RESULTS AND DISCUSSION

2.1 Homoselective Systems

From the polymerizable monomers of a technical C_4 fraction [23], only butadiene reacts via an anionic mechanism. By using suitable anionic initiators (naphthalene-Na, butyl-Li, modified Li-organic compounds, etc.) we obtained complete separation of butadiene from a C_4 fraction at room temperature in 60 min. Figure 1 shows GC-followed butadiene polymerization with the initiator butyl-Li. The C_4 fraction was dissolved in THF. The samples for GC detection were taken at constant pressure from the gas phase over the solution [24].

TABLE 1. GC Detected C–H Acidic Components of a Technical C_4 Fraction

Components	Concentration	
Acetylene	9.0 ppm	0.1×10^{-3} mol/L
Propadiene	0.20%	2.2×10^{-2} "
Propine	0.23%	2.6×10^{-2} "
Butadiene-1,2	608 ppm	6.9×10^{-3} "
Butine-1	618.7 ppm	6.9×10^{-3} "
Butine-2	22.0 ppm	0.25×10^{-3} "
Vinyl acetylene	2749.6 ppm	3.1×10^{-2} "
Pentadiene	7.0 ppm	0.8×10^{-4} "
	8314.3 ppm	0.0931 mol/L

It is known that Li-organic initiators in unpolar solvents show very low efficiencies [25] due to metalating side reactions and the formation of inactive associated species. By using C_4 fraction dissolved in unpolar solvents or liquefied without a solvent, the initiating efficiency rises more than 100% compared with pure butadiene. The high efficiency is most likely due to the strong π-donor capacity of the monoolefins which partially solvate the Li-organic compounds and reduces their association tendency.

Most important for high initiator efficiency, and with that a complete conversion of butadiene, is the purification of crude C_4 fractions. In Table 1 are listed the GC-detected C–H acidic components of a technical C_4 fraction.

The sum of C–H acidic compounds shows the same order as the concentration of the initiator normally used. To avoid a remarkable loss of active initiator, we used the combination of molecular sieve "Zeosorb 4 A," diethylaluminum ethoxide, and Li-butyl for purification. The known methods of selective hydrogenation would be preferred for technical processes [26]. From purified C_4 fractions we have realized a homoselective polymerization of butadiene with complete conversion by using different anionic or coordinative initiators [27]. The results are compiled in Table 2.

The time of reaction in order to get high conversions, or the molecular weights of the polymers as well as their microstructures, are nearly identical with the results of polymerizing pure butadiene in the solvents (cf. Table 2). In the same way as is valid for the polymerization of pure butadiene, the microstructure of the polymer changes depending on the nature of the initiator, the solvent, or the reaction temperature.

TABLE 2. IR Spectroscopical Detected Distribution of Microstructure for the Polymerization of Butadiene-1,3 from C_4 Fraction

Initiator	Solvent	Temperature (°C)	Microstructure distribution (%)		
			1,2-	1,4-trans-	1,4-cis-
Naphthaline-Na	THF	20	50-60	40-50	-
Butyl-Li	THF	20	80	20	-
Butyl-Li	Hexane	20	10	55	35
$V[C_6H_2(CH_3)_3]_3 \cdot 1.25$ THF	Benzene	20	30	35	35
$V[C_6H_2(CH_3)_3]_3 \cdot 1.25$ THF/AlBr$_3$	Benzene	20	10	15	75
$V[C_6H_2(CH_3)_3]_4$/ AlBr$_3$:					
Al:V ratio = 3	Benzene	27	-	55	45
Al:V ratio = 6	Benzene	27	-	67	33
Al:V ratio = 10	Benzene	45	-	100	-
$Li_2Cr_2(C_6H_5)_6 \cdot 1.5$ THF	Benzene	20	80	20	-

From the main components of the C_4 fraction, isobutene is the only monomer which can be polymerized via a cationic mechanism. With that, one has the possibility for selective polymerization of isobutene from the remaining fraction, which often is named the "butene fraction," by means of cationic initiators (Brönsted acids, Lewis acids). Evidently the cationic polymerization requires more effort than the anionic butadiene polymerization because butene-1 is a cationic polymerizing monomer and the trans- or cis-butene-2 shows isomerization or competition reactions in strong electrophilic media.

For oligomerization of isobutene from the butene fraction, in addition to specially prepared zeolites, solid complexes formed from metal sulfates (Me ≈ Al, Mg, Ca, V) and sulfuric acid were used [28].

The oligomerization was carried out from the gas phase at 20 to 100°C as well as from the liquefied butene fraction. Both reaction conditions predominantly yield dimers and trimers of isobutene. Conversion of isobutene and the homoselectivity have a strong dependence on the temperature of reaction and the amount of initiator used, as seen in Table 3.

TABLE 3. Gas-Phase Oligomerization of Isobutene from Butene Fraction Depending on Temperature and the Amount of Initiator

Temperature (°C)	Amount of initiator (g)	Remaining content (%)	
		Isobutene	Butene-1
Initiator: $MgSO_4/H_2SO_4/H_2O$			
25	3.0	32	100
50	1.5	45	100
50	3.0	20	90
75	3.0	25	70
98	1.5	25	65
98	3.0	18	40
Initiator: $VOSO_4/H_2SO_4/H_2O$			
25	1.5	100	100
25	3.0	80	100
50	1.5	80	100
50	3.0	55	90
75	1.5	80	100
75	3.0	25	100
98	1.5	75	100
98	3.0	18	60

GC analysis does not allow separate determination of isobutene and trans-butene-2, thus the data in Table 3 obtained at 98°C mean a complete isobutene conversion. Whereas the $MgSO_4$ initiator (Table 3) forms nearly 50% dimers besides low amounts of codimer with butene-1 (increasing with an increase of temperature or concentration of the initiator) and 45 to 50% trimers, the $VOSO_4$ initiator shows higher homoselectivity, whereas in the temperature range 25 to 50°C about 80% dimers and 15 to 20% trimers are formed. The GC-detected ratio of the two dimers, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, was 4:1, corresponding to the data published by Kennedy [29] for the dimerization of pure isobutene. The isobutene conversion was very important for the exclusion of butadiene traces which are present in technical butene fractions after extractive separation of butadiene from the C_4 fraction. Figure 2 shows how the GC-detected isobutene conversion depends on different amounts of butadiene. The retarding
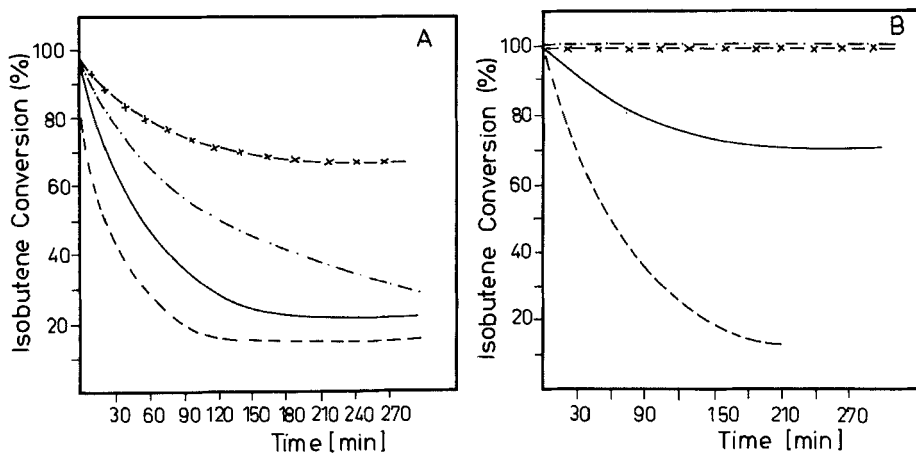
FIG. 2. Effect of butadiene on the conversion of isobutene oligomer-ization from olefin mixtures. Temperature: 50°C. (A) Initiator: $MgSO_4/H_2SO_4/H_2O$. (B) Initiator: $VOSO_4/H_2SO_4/H_2O$. Composition of the mixtures: (- -) 55 mL isobutene, 25 mL butene-1, 20 mL n-butane; (——) 100 mL butene fraction (1 to 2% butadiene); (- •) 95 mL butene fraction, 5 mL butadiene; (×) 100 mL C_4- fraction (35% butadiene).

effect of butadiene seems to be due to proton transfer because non-propagating species are formed [30].

In order to realize selective polymerization of isobutene leading to high molecular weights, Lewis acids must be used for initiation instead of Brönsted acids. Strong Lewis acids (e.g., $AlCl_3$) show high cationic activity but a smaller homoselectivity relative to isobutene polymerization. We found suitable initiators for selective isobutene polymerization by using Lewis acid mixtures ($TiCl_4/AlBr_3$, $SbCl_5/AlBr_3$). They were also used by Marek and co-workers [31, 32] for polymerization of pure isobutene. High molecular weights (> 100,000) require superpurification procedures of the butene fraction, whereas the C–H acidic components mentioned in Table 1 must be excluded, as well as traces of butadiene.

In Fig. 3 is shown isobutene polymerization from a butene fraction obtained with a $TiCl_4/AlBr_3$ mixture in hexane as solvent. The non-reacting portion of the butanes serves as an internal standard for GC analysis. While the isobutene/butanes ratio decreases with time, the butene-1/butanes ratio remains constant, corresponding to the homo-selectivity of the system [33].

Figure 4 shows that the optimized yields of precipitable polyiso-butene (PIB) require a nearly 60:1 ratio of the two-component initiator $TiCl_4/AlBr_3$.

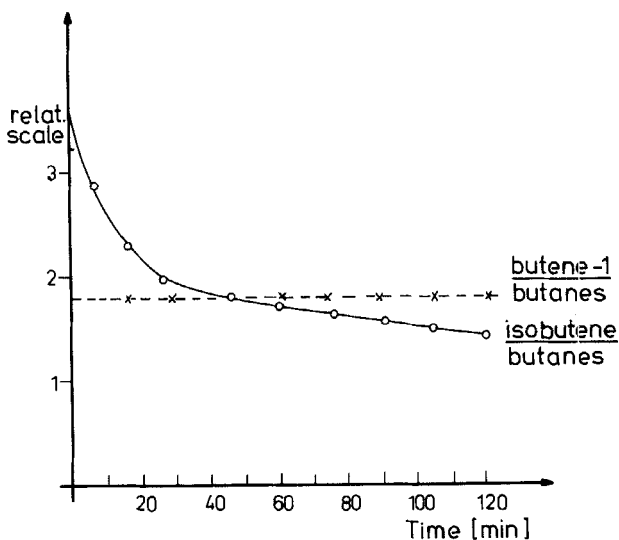As is to be expected [34], the yield of PIB, the molecular weight,

FIG. 3. Time-dependent selective polymerization of isobutene
from the butene fraction by gas chromatography. Initiator: $TiCl_4$/
$AlBr_3$ (60:1; total concentration 10^{-3} mol/L). Solvent: Hexane.
Temperature: 20°C.

and the MW distribution (MWD) are affected by the temperature and
the initiator concentration, therefore suitable variations of the reac-
tion conditions allow the yield of products with special properties
[35]. Figure 5 visualizes the dependence of precipitable PIB yield
on temperature and initiator concentration.

The PIB were also analyzed by H-NMR spectroscopy with refer-
ence to butene-1 participation in the polymerization. With increasing
temperature as well as increasing concentration of the initiator, the
homoselectivity decreases, but we have never found more than 10%
butene-1 participation, even under unfavorable conditions. The effect
of the initiator concentration on the molecular weight is shown in
Fig. 6. The difference between the two curves represents the un-
homogeneity $[U = (M_w/M_n) - 1]$ of the polymer. The value of U in-
creases with increasing concentration.

In line with the known decrease of molecular weight in cationic
polymerization due to increasing the temperature of the reaction,
this effect has also been found for selective polymerization. High
molecular weight PIB ($M_n > 20,000$) was only obtained below -50°C.
As is to be expected, with increasing temperature the MWD curves
are broadened and the maximum changes to low molecular weights.

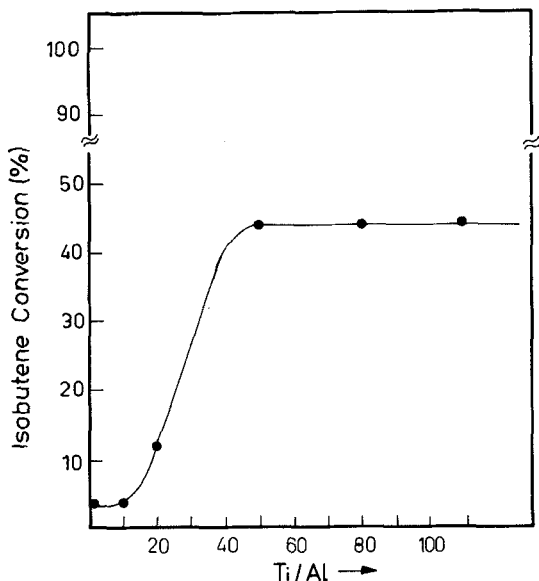In a series of papers, Italian workers reported successful isobutene

FIG. 4. Effect of Ti:Al ratio on the conversion of isobutene using TiCl₄/AlBr₃ for the selective polymerization from the butene fraction. [AlBr₃] = 4×10^{-4} mol/L. [Isobutene] $\approx$ 40 vol%. Temperature: $-78°C$. Time of reaction: 120 min.

polymerization to obtain high molecular weights by using two component initiators (alkylaluminums/organic electron acceptors) [36-41]. We found these initiators also to be suitable for the selective polymerization of isobutene from the butene fraction, for we obtained relative high molecular weight PIB (depending on temperature) and complete conversion within a short reaction time. Figure 7 shows the results obtained with Et₂AlCl/tetracyanonaphthoquinone (TCNNQ) as the initiator.

In addition to GC detection of homoselective polymerization (Fig. 7), NMR spectroscopic analysis of the products also showed that butene-1, within experimental error, did not take part in the reaction.

Both types of initiators (TiCl₄/AlBr₃ and Et₂AlCl/TCNNQ) show a similarity due to their ability to stabilize anions by complex formation with acceptors [42, 43]. In earlier papers the authors [42-44] proposed "acceptor-stabilized" counterions which have a lower nucleophilicity. Thus the propagation reaction in cationic polymerization is favored in comparison with chain limiting or other competing reactions. The formation of stabilized counterions may be explained by the following scheme:
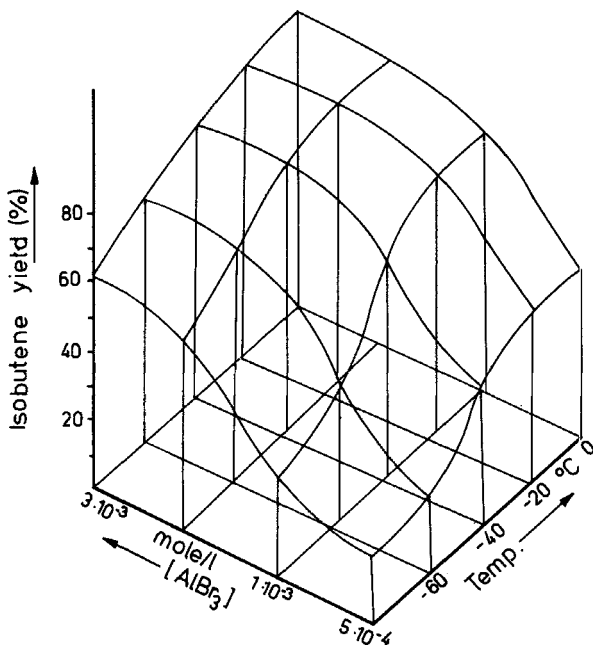
FIG. 5. Dependence of yield of selective isobutene polymerization from the butene fraction as a function of temperature and the initiator concentration (TiCl$_4$:AlBr$_3$ = 60:1).

$$C^{\oplus}[AlBr_3X]^{\ominus} + TiCl_4 \xrightleftharpoons{K_{EDA}} C^{\oplus} + [AlBr_3X]^{\ominus} \cdots \cdots \blacktriangleright TiCl_4$$

$$C^{\oplus}[AlEt_2ClX]^{\ominus} + TCNNQ \xrightleftharpoons{K_{EDA}} C^{\oplus}$$

$$+ [AlEt_2ClX]^{\ominus} \cdots \cdots \cdots \blacktriangleright TCNNQ$$
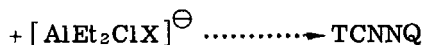
where X is OH or halogen.

After the separation of butadiene via an anionic mechanism and iso-butene via a cationic mechanism, the principle of reactive separation by selective polymerization reactions can be extended to butene-1. Using strong Lewis acids (e.g., AlCl$_3$ in dichloroethane) as initiators, butene-1 was polymerized from the remaining butene fraction, but only low molecular weight products were obtained. According to ^{13}C-NMR-spectroscopic data recently published [45], the structures of these
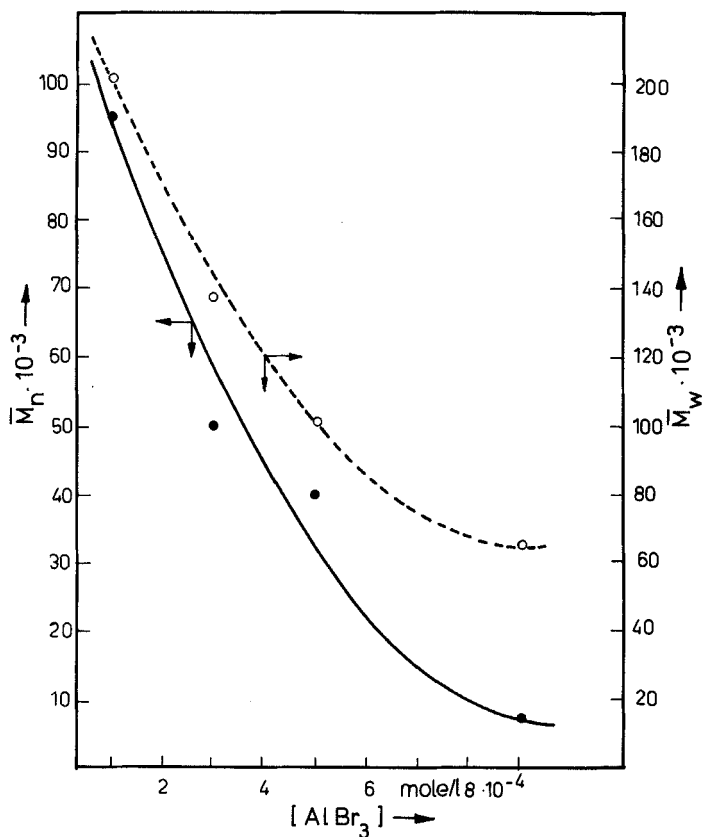
FIG. 6. Effect of initiator concentration on the average molecular weight of polyisobutenes, with $TiCl_4/AlBr_3$ (100:1) as the initiator. Reaction conditions as in Fig. 4.

products were found to be strongly unhomogeneous. On the other hand, selective butene-1 polymerization could be realized with the help of heterogeneous Ziegler-Natta initiators. High yields were obtained with γ-$TiCl_3$/AlEt$_3$ at 70°C, carried out in an autoclave, without additional solvent. In the case of a butene-1/TiCl$_3$ ratio of 800:1, the polymers show 75% isotactic structures after extraction with ether. In sum, the polymerizable components of a C_4 fraction have been polymerized stepwise by changing the mechanism of the polymerization reaction. The unreacting olefins and alkanes might be used for alkylation, oxidation, or some other reactions.

FIG. 7. GC analysis of selective isobutene polymerization from the butene fraction with the initiator $AlEt_2Cl/TCNNQ$ (1.77×10^{-2} mol/L/6.83×10^{-5} mol/L) in CH_2Cl_2 at -50°C. (1) Isobutene, (2) butene-1, (3) n-butane, (4) isobutane, (5) trans-butene-2, (6) cis-butene-2.

2.2. Coselective Systems

Extending this concept, new products with special properties are obtainable by selective copolymerization.
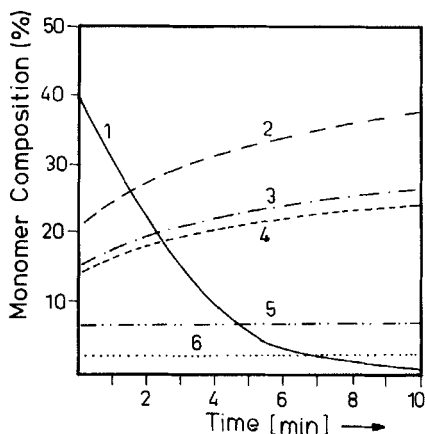
By use of the three component initiator $Al(i-Bu)_3/I_2/TiCl_4$ to investigate the copolymerization of cyclopentadiene and monomers of a C_4 fraction, the results listed in Table 4 were obtained.

Although with this initiator system no correct coselectivity of both dienes has been realized, the last column in Table 4 shows a remarkable decrease of the isobutene or butene-1 participation. These findings might be due to the low concentration of the stronger Lewis acid $TiCl_4$ and, with that, a decrease of the "cationic activity" of the initiator system. The copolymerization of cyclopentadiene and butadiene seems to be favored via a "more coordinative" mechanism.

More significant results were obtained by investigating the copolymerization of α-methylstyrene and isobutene from a butadiene-free butene fraction. Suitable initiators were the two-component systems mentioned in Section 2.1 ($AlBr_3/TiCl_4$ and $Et_2AlCl/TCNNQ$) as well as different syncatalytic systems ($Et_2AlCl/t-BuCl$ and Et_2AlCl/Cl_2) reported by Kennedy and co-workers [22, 29, 34, 46, 47]. Table 5 lists yields, molecular weights, and copolymer compositions obtained using the $TiCl_4/AlBr_3$ (60:1) system in the range from -30 to -78° C.

The composition of the copolymer changes with variations in the temperature and/or the initiator concentration. The amount of isobutene

TABLE 4. Copolymerization of Cyclopentadiene with Monomers from a C_4 Fraction Using $Al(i-Bu)_3/I_2/TiCl_4$ Initiator[a]

	Monomer conversion (mol%) at the initiator ratio of			
Monomers	11:5:11	16.5:7.5:16.5	22:10:22	22:10:5.5
Isobutene	57.6	61.9	54.3	10.0
Butadiene-1,3	37.6	33.0	32.0	24.6
Butene-1	33.0	38.5	37.0	14.0
Total yield (mg)	4800	4870	4560	3340

[a]Experimental conditions: 6 g C_4 fraction (9.6 mL); cyclopentadiene, 2.64 g = 0.8 mol/L; solvent, benzene (40.4 mL); temperature = 10°C; time = 120 min; $Al(i-Bu)_3:I_2:TiCl_4$ = 6.4 × 10^{-3} mol/L:2.8 × 10^{-3} mol/L:6.4 × 10^{-3} mol/L, adequate to 11:5:11.

in the copolymer increases, with increasing reactivity, but the raw product becomes more and more soluble in hexane, which suggests increasing homopolymerization with the formation of longer isobutene block sequences in the copolymer. Similarly, the molecular weight decreases with increasing reactivity and inhomogeneity grows in the same direction (Table 5). GC analysis of the remaining butene fraction shows that butene-1 does not take part in the reaction under the conditions investigated.

Using the different types of initiators shown in Table 6, despite their higher reactivity, the molecular weights are in the same range or somewhat higher compared with the $TiCl_4/AlBr_3$ system, and the solubility of the copolymers in hexane is very low.

From an H-NMR spectroscopic comparison of the copolymers (Tables 5 and 6), it is concluded that the products initiated with $TiCl_4/AlBr_3$ show a higher amount IB triades whereas in the case of initiation with $Et_2AlCl/t-BuCl$ the mixed triades IB/α-MeS increases [48]. The change of the coselectivity (compare k_{12} and k_{21} in Section 1) as well as the relative high molecular weights lead to the conclusion that the particularities of the syncatalytic systems (Table 6) cannot only be explained by the difference in initiation compared with conventional Lewis acids. Obviously, thermodynamic stabilization of the counterions is favored, as mentioned in Section 2.1, and so is propagation of the crossed propagation reaction. In both cases (Tables 5 and 6) the participation of butene-1 was excluded by GC analysis.

For the selective copolymerization of butene-1 with other monomers, good results were obtained via a coordinate mechanism. Using the classical Ziegler-Natta initiator $TiCl_4/Et_2AlCl$, selective copolymerization between norbornene and butene-1 was obtained. The reactions

TABLE 5. Selective Copolymerization of Isobutene (IB) with α-Methylstyrene (α-MS) from Butene Fraction Using the Initiator $TiCl_4/AlBr_3$ (60:1); Time of Reaction 60 min

[IB] (mol/L)	[α-MS] (mol/L)	[TiCl$_4$] (mmol/L)	[AlBr$_3$] (mmol/L)	Temperature (°C)	Yield (%)[a]	Conversion of IB (%)[b]	M_n ^{c} ×10^{-3}	U[d]	IB content[e] in the copolymer (mol%)
0.85	0.85	10.1	0.17	-78	26	14	6.6	0.63	2.5
0.85	0.85	20.2	0.34	-78	62	23	5.2	0.79	18.4
0.85	0.85	40.4	0.68	-78	100	100	4.6	0.71	29.5
0.85	0.85	60.6	1.02	-78	100	100	3.8	0.98	27.8
1.70	0.85	10.1	0.17	-78	18	3	8.1	0.66	10.0
1.70	0.85	20.2	0.34	-78	35	14	8.0	0.71	17.0
1.70	0.85	40.4	0.68	-78	91	89	6.5	1.00	29.7
1.70	0.85	60.6	1.02	-78	99	98	4.8	1.02	35.5
1.70	0.43	40.4	0.68	-78	71	85	0.6	1.00	31.5
0.85	0.85	40.4	0.68	-50	98	100	1.7	2.8	50
0.85	0.85	40.4	0.68	-30	91	100	0.6	3.0	14.5

[a] Precipitable product, due to the total amounts of IB and α-MS.
[b] GC analysis.
[c] Means copolymer extracted in boiling hexane; M_n detection by GPC in THF, using polystyrene as standard.
[d] Unhomogeneity: $U = (M_w/M_n) - 1$.
[e] Detected by H-NMR spectroscopy.

TABLE 6. Selective Copolymerization of Isobutene (IB, 0.85 mol/L) with α-Methylstyrene (α-MS, 0.85 mol/L) from Butene Fraction Using the Initiator $AlEt_2Cl$/Acceptor $AlEt_2Cl$/t-BuCl[a]

Acceptor t-BuCl	$\dfrac{[\text{Acceptor}]}{[\text{t-BuCl}]}$	Temperature (°C)	Yield (%)	Conversion of isobutene (%)	$M_n \times 10^{-3}$	U	IB content in the copolymer (mol%)
Chloranil	0.115	-50	48.0	7	2.3	1.72	3
TCNE	0.115	-50	58.3	21	3.6	1.18	7
TCNQ	0.115	-50	56.8	35	2.3	1.61	16
TCNNQ	0.115	-50	73.4	93	2.6	1.81	30
TCNNQ	0.172	-50	83.3	95	2.5	1.78	38
TCNNQ	0.230	-50	85.1	98	2.1	1.68	40
t-BuCl	2.04	-78	50.9	18	12.7	0.87	4
t-BuCl	2.04	-30	50.0	23	4.6	0.90	2
t-BuCl	5.10	-78	98.9	100	8.1	1.71	30
t-BuCl	5.10	-30	99.5	100	5.6	1.56	44
t-BuCl	5.10	-10	93.0	100	3.0	1.40	50

[a]Solvent, CH_2Cl_2; $[AlEt_2Cl] = 22.2$ mmol/L; time of reaction, 30 min. Recording of data same as in Table 5.
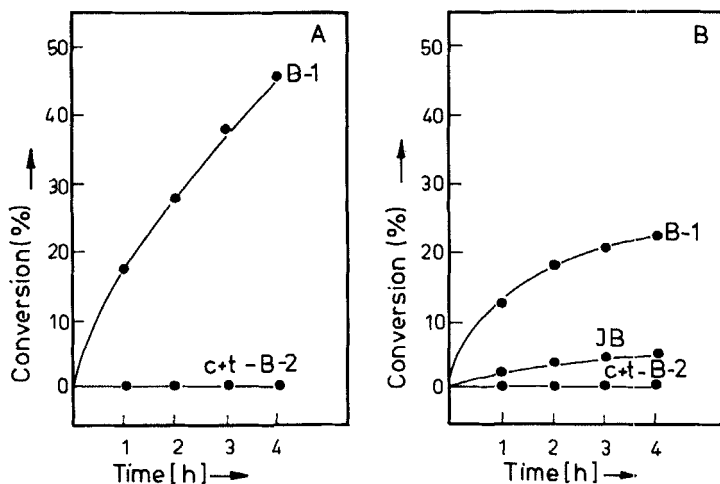
FIG. 8. GC detected conversion of C_4-olefins for the selective co-polymerization of butene-1 (B-1) with norbornene (N), using $TiCl_4/$ $AlEt_2Cl$ initiator in heptane at $80°C$. (A) Using the isobutene-free fraction. (B) Using the butene fraction with 40 vol% isobutene. Concentrations for A: $[B - 1] = 1.22$ mol/L, $c + t - [B - 2] = 0.73$ mol/L, $[N] = 4.73$ mol/L, $[initiator] = 20.0$ mmol/L. Concentrations for B: $[B - 1] = 0.48$ mol/L, $c + t = [B - 2] = 0.10$ mol/L, $[N] = 4.73$ mol/L, $[initiator] = 20.0$ mmol/L.

were carried out in an autoclave at $80°C$. Figure 8 shows the remark-able effect of isobutene on coselectivity.

Whereas with an isobutene-free fraction the system behaves co-selectively and there are no participation or isomerization reactions of the two butene-2s according to GC analysis (Part A in Fig. 8), the coselectivity decreases if isobutene is present (Part B in Fig. 8).

It is of interest that under suitable conditions selective copolym-erizations of butene-1 with other vinyl-type monomers were obtained via a radical mechanism. Japanese workers [49] studied the radical copolymerization of VAc with different pure C_4 olefins. They found the following sequence of decreasing reactivity: butene-1 $\gg$ isobutene $>$ trans-butene-2 $\approx$ cis-butene-2.

In our experiments, selective copolymerization of butene-1 with VAc was only obtained using an isobutene-free fraction. Otherwise, due to high termination or transfer reactions of isobutene, only oligomers were formed. Data for the selective copolymerization of butene-1 with VAc prepared using diisopropyl peroxidicarbonate (DIPP) are given in Table 7. The 2-butenes remain unreacted.

TABLE 7. Selective Copolymerization of Butene-1 (B-1) with Vinyl
Acetate (VAc) from Isobutene-Free Butene Fraction (time of reaction
= 6 h, temperature = 60°C)

$\dfrac{VAc}{B-1}$	$[DIPP]^a$ (vol%)	Yield[b] (%)	Content of B-1[c] in the copolymer (mol%)	$M_n^d \times 10^{-3}$
0.95	0.1	2.8	23	1.0
1.5	0.1	4.3	17	1.3
2.6	0.1	8.3	9	5.8
4.0	0.1	11.5	10	21.9
5.85	0.1	15.8	12	19.5
12.4	0.1	31.4	5	30.7
4.0	0.025	2.4	0	-
4.0	0.050	5.8	13	24.5
4.0	0.1	11.5	10	21.9
4.0	0.15	19.8	11	20.2
4.0	0.25	27.9	10	16.5
4.0	0.5	48.2	13	7.4

[a]DIPP = diisopropyl peroxydicarbonate.
[b]Due to the total amounts of B-1 and VAc.
[c]Detected by H-NMR spectroscopy.
[d]Detected by osmometry.

3. GRAFTING BY SELECTIVE POLYMERIZATION

Kennedy and co-workers studied in detail the formation of graft
copolymers onto chlorinated polymers using weak Lewis acids (alkyl-
aluminum compounds), whereas by the use of strong Lewis acids the
grafting efficiency has been found to be rather poor [50, 51]. We
have applied this method for grafting of butadiene and isobutene onto
chlorinated polymers [52-55] with olefin mixtures taken as the
sources of the graft component. In the case of butadiene the micro-
structure of the grafted chains had a preference for the 1,4 connec-
tion; there was also a small amount of the 1,2 structure (Table 8).
By the use of a two-component initiator consisting of Et₂AlCl and
complex compounds with Co or Ni, increasing graft yields were
obtained and the cis-1,4 microstructure of the grafted chains increased

TABLE 8. Stereospecificity of Butadiene-1,3 Grafting onto Chlorinated Polycyclopentadiene (CPCPD) (solvent, chlorobenzene; butadiene-1,3 amount, 20 g/L; Cl content of the CPCPD $\approx$ 46.3 mass%; time of reaction, 60 min)

Temperature ($^\circ$C)	Initiator concentration (mol/L)	Grafting efficiency (%)	Microstructure distribution (%)		
			1,4-cis	1,4-trans	1,2-
-20	AlEt$_2$Cl $= 3 \times 10^{-2}$	53	51	45	4
-10	AlEt$_2$Cl $= 3 \times 10^{-2}$	55	71	27	2
25	AlEt$_2$Cl $= 3 \times 10^{-2}$	56	83	16	1
-20	AlEt$_2$Cl $= 3 \times 10^{-2}/$ [Co(salicyl-aldehyde-imine)$_2$] $= 2.7 \times 10^{-3}$	81	91	4	5
-20	AlEt$_2$Cl $= 4 \times 10^{-2}/$ [Co(acetyl-acetonate)$_2$] $= 3.2 \times 10^{-3}$	80	90	6	4
-20	AlEt$_2$Cl $= 5.25 \times 10^{-2}/$ [Co(acetyl-acetonate)$_3$] $= 3.4 \times 10^{-3}$	83	87	10	3

up to 90%. As an example, Table 8 shows the results of butadiene grafting onto chlorinated polycyclopentadiene [55]. These grafted products are rubberlike in behavior. By using a purified C$_4$ fraction instead of pure butadiene, selective graft copolymerization led to the same microstructure, only the total yield as well as the grafting efficiency were slightly reduced.

Grafting of isobutene onto chlorinated polymers with Et$_2$AlCl requires higher initiator concentrations as well as higher temperatures [56, 57]. Therefore we used different alkylaluminums with stronger Lewis acidities (EtAlCl$_2$, Et$_3$Al$_2$Cl$_3$, AlCl$_3$) as initiators for grafting onto chlorinated polycyclopentadiene or different types of chlorinated PVC (Cl content 40 to 63%). Dichloromethane was the solvent; in some cases (Et$_3$Al$_2$Cl$_3$) cyclohexane was used. Graft reactions initiated with EtAlCl$_2$ or AlCl$_3$ were unsatisfactory, independent of the use of pure isobutene or a purified butene fraction for the experiments. Only with Et$_3$Al$_2$Cl$_3$ were graft products obtained (between 15 to 25% grafting efficiency; see Table 9), besides a remarkable amount of PIB.

TABLE 9. Grafting of Isobutene from Butene Fraction onto Chlorinated Polycyclopentadiene (CPCPD) in CH_2Cl_2 at $-15°C$. (Butene fraction, 20 mL (40% isobutene); time, 60 min; CPCPD (45 mass% Cl) = 5 g in 200 mL solvent)

Initiator	Concentration of initiator (mol/L)	Total yield (g)	Graft product (g)	Grafting efficiency (%)
$Et_3Al_2Cl_3$ [a]	0.01	6.0	1.0	16.6
$EtAlCl_2$ [a]	0.01	5.2	0.2	3.8
$Et_3Al_2Cl_3$ [b]	0.01	6.5˙	1.5	23.1
$AlBr_3$	0.01	7.1	2.1	29.5
$SnCl_4$	0.01	6.8	1.8	26.4
$TiCl_4/AlBr_3$ (60:1)	0.01	8.7	3.7	42.5

[a] Carried out with pure isobutene (10 g IB, 5 g CPCPD, 100 mL CH_2Cl_2) at $-20°C$.
[b] Solvent cyclohexane; other conditions same as footnote a.

TABLE 10. Isobutene Grafting onto Polyphenyl Vinyl Ether (PPhVE)

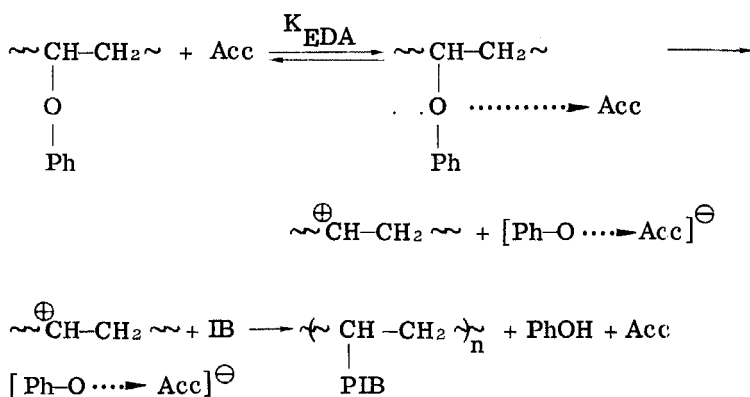| Comonomer	Initiator	Time (h)	Conversion of comonomer (%)	Comments
Isobutene	$SnCl_4$	1	36.1	87% PIB[a]
Butene fraction (40% isobutene)	$SnCl_4$	1	10.7	45% PIB
Isobutene	Chloranil	4	12.3	15% PIB
Isobutene	Et_3Al (1×10^{-3} mol/L)	4	4.1	40% unsoluble[b]
Isobutene	Et_3Al (5×10^{-3} mol/L)	4	5.3	48% unsoluble
Isobutene	Et_3Al (1×10^{-2} mol/L)	4	9.1	64% unsoluble

[a] PIB = polyisobutene, extracted with pentane from the graft product.
[b] Product insoluble in organic solvents.

Grafting efficiencies obtained with $Et_3Al_2Cl_3$ in cyclohexane solvent at -20°C increased (up to 60%) when the initiator was slowly dropped into the reacting system. Even the grafted products were soluble in $HCCl_3$ and showed a higher thermal stability, in general. They were more or less colored (light brown to ochre).

More successful were the experiments using conventional but relatively weak Lewis acids. Table 9 shows the results of selective isobutene grafting onto chlorinated polycyclopentadiene. As reported in Sections 2.1 and 2.2, again the mixture of the two Lewis acids $TiCl_4$ and $AlBr_3$ showed the highest grafting efficiency and correct homoselectivity due to isobutene, detected by GC. Nevertheless, PIB was also formed by chain transfer.

Similar results have been observed by grafting of isobutene onto polyphenyl vinylether (PPhVE) using weak Lewis acids or organic π-acceptors as initiators for the intermediate formation of carbenium ions at the backbone [58]:

$$\sim CH-CH_2\sim \; + \; Acc \; \underset{}{\overset{K_{EDA}}{\rightleftharpoons}} \; \sim CH-CH_2\sim \longrightarrow$$

$$\begin{array}{ccc} | & & | \\ O & & .\,.O \cdots\!\!\blacktriangleright Acc \\ | & & | \\ Ph & & Ph \end{array}$$

$$\overset{\oplus}{\sim}CH-CH_2\sim \; + \; [Ph-O\cdots\!\!\blacktriangleright Acc]^{\ominus}$$

$$\overset{\oplus}{\sim}CH-CH_2\sim + \; IB \; \longrightarrow \; \curlyvee CH-CH_2\curlyvee_n \; + \; PhOH + Acc$$

$$[Ph-O\cdots\!\!\blacktriangleright Acc]^{\ominus} \qquad\qquad PIB$$

The results with isobutene (pure or from butene fraction) using different types of initiators ($SnCl_4$, Et_3Al, chloranil) in CH_2Cl_2 solvent are compiled in Table 10.

By extraction with pentane, the graft polymers prepared with $SnCl_4$ show relatively high amounts of PIB. These were decreased by using π-acceptors, but could not be suppressed. According to Table 10, Et_3Al, which cannot initiate cationic polymerization, is operative for grafting. Increasing the initiator concentration increases the grafting efficiency [58] but formation of insoluble products also increases.

4. SUMMARY

Mainly by the use of technical C_4 fractions (butene fractions), the reactive separations of olefins by selective polymerization reactions have been described. The general suppositions for the realization of

homo- or coselective systems have been reported, and the particular aptitude of ionic or coordinative chain propagation mechanisms has been emphasized. The complete utilization of a C_4 fraction was shown, changing step by step the nature of the mechanism or the relative reactivity of different monomers within one mechanism. Examples for variation of product properties were shown by controlling the microstructure, the molecular weights or MWD, or the composition of the copolymers. The palette of new products has been extended by selective copolymerization of C_4 olefins with monomers from higher pyrolysis fractions or by selective grafting when olefin mixtures as monomer sources were used.

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