Translated from *Uspekhi Khimii*, **54**, 1208 - 1229 (1985) U.D.C. 678.742.4

Functional Derivatives of Polyisobutene

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The methods of synthesis of isobutene polymers with end groups of different types are examined. It is shown that advances in the synthesis of these compounds are associated with the progress in the field of the regulation of the cationic polymerisation and copolymerisation of isobutene and the degradation of isobutene polymers and copolymers. Examples of the employment of functional derivatives of isobutene polymers in various branches of technology are presented. The bibliography includes 102 references.

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I. INTRODUCTION

Polyisobutene (PIB) and its copolymers (PIBC) together with dienes occupy an outstanding position among polyolefins as regards the volume in which they are manufactured and used. This is due to the availability of the raw materials and the valuable properties of the polymer. "Defect-free" PIB molecules exhibit a relatively high resistance to chemical and physical influences and are irreplaceable as corrosion resistant hermetic sealing compounds, additives, oils, and other materials.[1] On the other hand, the chemical inertness of PIB hinders the introduction of functional groups into the polymer chain. It is known that the introduction of such groups significantly expands the applications of hydrocarbon elastomers to which PIB also belongs.[2]

During the last 5–10 years numerous publications devoted to the synthesis of PIB with specified end groups by the cationic polymerisation of isobutene (IB), oxidative degradation of PIBC with dienes, and other procedures have appeared. The introduction of reactive groups into PIB and their subsequent reactions lead to the formation of products with polar groups, for example, with antioxidant fragments, graft and block copolymers, etc. i.e. to the variation of the properties of PIB over a wide range of molecular weights. This leads to new applications of PIB.

The aim of this review is the systematic account and a survey of the literature data concerning the method of synthesis of functional derivatives of PIB with specified end groups and new applications of the modified PIB.

II. METHODS FOR THE INTRODUCTION OF FUNCTIONAL GROUPS INTO ISOBUTENE POLYMERS DURING POLYMERISATION

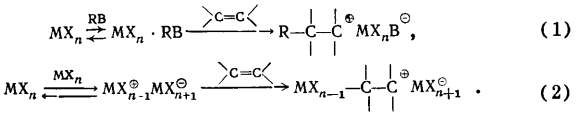
Until recently it was believed that the PIB obtained by the polymerisation of IB under the influence of acid catalysts contain mainly t-butyl and unsaturated fragments at the end of the chain.[3] However, the latest investigations of the low-temperature cationic polymerisation of IB in the presence of complex catalysts and (or) specially introduced additives indicated the possibility of forming PIB with end groups different from those indicated above.[4] Here and henceforth these products are treated as functional derivatives of PIB. In terms of their origin, the end groups in PIB can be divided by convention into "head" groups (formed in the polymer chain initiation and transfer stages), and "tail" groups (formed in chain termination steps). Serious obstacles to the introduction of functional groups into PIB during the cationic polymerisation of IB arise from the high reactivity of the intermediate carbonium ions, the high fluidity, and the difficulty of controlling the PIB formation processes. The short lifetime of the carbonium ion centres rules out the possibility of polymerisation via the "living chain" mechanism,[5] which is the traditional method for the introduction of tail functional groups into polymers based on anionically active monomers.[6,7]

The synthesis of PIB with specified end groups was a consequence of a deeper understanding of the mechanism of the cationic polymerisation of IB and, in particular, of the chemistry of the chain initiation and termination reactions, as well as the application of modern methods for the quantitative analysis of polymers.

In contrast to Brønsted acids, which lead to the formation of low-molecular-weight products alone[3] and carboxylate salts which are relatively inactive in polymerisation,[4] Lewis acids and complexes based on them show a high reactivity in the polymerisation of IB, creating difficulties in the regulation of the process as a whole and of its individual elementary stages.

When strong Lewis acids (MX_n) are used as the catalyst, their interaction with the monomers and additives (the cocatalyst RB) determines the different initiation pathways and hence also the nature of the head groups (Scheme 1).

Scheme 1



(1)

(2)

Depending on the pathway in the polymerisation initiation reaction, the initiator fragments R or MX_{n-1} are introduced into the chain with formation of alkyl (phenyl) PIB derivatives [reaction (1)] or polymeric organometallic compounds [reaction (2)] respectively. The predominance of a particular reaction pathway depends on the nature of the Lewis acid, the cocatalyst, their concentrations, and the polymerisation conditions.[4] As a rule, these reactions occur under conditions which absolutely rule out the presence of traces of proton-donating compounds in the system. However, such purity has been achieved only in isolated studies using

special vacuum apparatus and the most sophisticated experimental techniques.[4,8,9] In the polymerisation of IB in the presence of traditional catalysts ($AlCl_3$ and BF_3 containing admixtures of proton donors HB) the head t-butyl groups are formed both in the initiation of the process by protons [reaction (1)] and in the chain transfer to the monomer [reaction (2)] while the tail C–C bonds arise only in the chain termination by reactions (3) (Scheme 2).

Scheme 2

$$HB + MX_n + C_4H_8 \rightarrow \quad t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus}, \qquad (1)$$

$$t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus} + nC_4H_8 \rightarrow \quad t\text{-}C_4H_9(C_4H_8)_n^{\oplus}MX_nB^{\ominus}, \qquad (2)$$

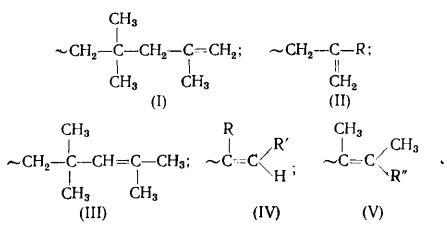
$$t\text{-}C_4H_9(C_4H_8)_n^{\oplus}MX_nB^{\ominus} + C_4H_8 \rightarrow \quad t\text{-}C_4H_9(C_4H_8)_kC_4H_7 + \quad t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus}, \qquad (3)$$

where reactions (1), (2), and (3) are elementary initiation, propagation, and termination steps and $k = n - 1$.

Since reactions (1) and (3) take place even when aprotic cocatalysts are used (Cl_2, RCl, etc.[4]), the introduction of head groups other than t-butyl groups into PIB presents certain difficulties associated both with the elimination of the influence of proton-donating impurities and with the selection of catalytic systems or additives which prevent chain transfer to the monomer.

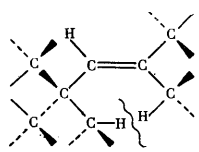
Bearing in mind the decisive contribution of the polymer chain termination reaction to the formation of head and tail groups in PIB,[9,10] it is useful to consider the characteristic features of this reaction.

A characteristic feature of the cationic polymerisation of IB in the presence of the majority of acid catalysts is intense chain transfer to the monomer [reaction (2), Scheme 2].[8] Quantitative and qualitative analysis of the end groups in PIB established that on average there is one C=C bond per macromolecule.[11,12] According to ^1H NMR data,[12] the unsaturated groups in PIB can be represented by structures (I)–(V) with structures (III) and (IV) predominating:



These results significantly supplement and correct the investigations in which mainly vinylidene C=C bonds were detected by infrared spectroscopy.[13]

The ratio of trisubstituted and vinylidene C=C bonds in IB dimerisation and trimerisation processes is probably controlled by steric factors.[9] The transition state in the formation of structure (III) is slightly compressed owing to the interaction of the hydrogen atoms of the methyl groups not linked by chemical bonds:



The two hydrogen atoms shown below this scheme tend to approach one another as soon as a double bond is formed. In contrast to this, the transition state in the formation of structure (I) is much less deformed, which compensates for the difference between the heats of formation of the olefins. When the internal stress cannot be relieved by the rotation of the interaction groups, compound (I) is formed in this case as the main product (Table 1).

Table 1. Characteristics of unsaturated PIB.

Catalyst + additive	M_n^*	Content of C=C bonds, % of theoretical		Method of determination**	Refs.
		tri-substituted	vinylidene		
H_2SO_4(KY-2)	412	20	80	1	[9]
$CuSO_4$·HCl	468	60	40	1,3	[10]
$CaSO_4$·CCl_3CO_2H	880	46	45	1	[12]
BF_3	1950	46	30	1	[12]
BF_3·CH_3COOH	590	40	29	1	[12]
BF_3·H_2O	970	51	13	1	[12]
$AlCl_3$	770	67	9	1,2	[12]
RCl–BCl_3–$CH_3CN(C_4H_9)_2$	500	0	100	1	[14]

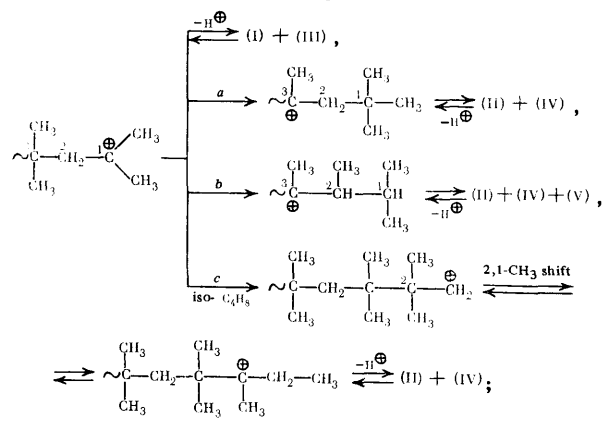
*M_n represents the number-average molecular weights of the PIB.

**1) ^1H NMR; 2) infrared spectroscopy; 3) ozonolysis.

Depending on the polymerisation conditions and the nature of the catalysts, the ratio of the trisubstituted and vinylidene double bonds in PIB varies within wide limits.

Compounds (I) and (III), formed initially in the PIB obtained in the presence of BF_3, can probably undergo a skeletal rearrangement and isomerisation to compounds (II), (IV), and (V) (Scheme 3, *a* and *b*), which agrees with the results of studies of the model system tri-isobutylene + $AlBr_3$ + DBr.[15] The conclusion that compound (V) is formed is based on the fact that the unsaturation detected by ^1H NMR (which is insensitive to tetrasubstituted C=C bonds) is much less marked than the unsaturation measured by hydrogenation methods. The low content of vinylidene C=C bonds and the predominance of compound (IV) among the trisubstituted olefins in the PIB obtained in the presence of $AlCl_3$ are probably associated with multistage polymer chain termination. According to Puskas et al.[12] and Slobodin and Matusevich,[16] it includes the anomalous "tail to tail" addition of isobutene and the subsequent methyl shift (Scheme 3, *c*).

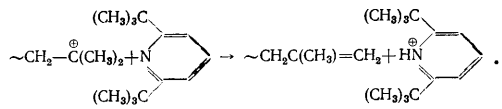
Scheme 3



a) 1,3-CH_3 shift; *b*) 1,2-H and 1,2-CH_3 shifts; *c*) anomalous "tail to tail" addition of isobutene; the symbol ~ denotes the PIB chain.

The anomalously high content of compound (I) in the PIB obtained in the presence of 2,6-di-t-butylpyridine (Table 1) is a consequence of the complete suppression of the reaction involving chain transfer to the monomer. The aromatic base then serves as a kind of trap,[17,18] which selectively abstracts a proton from the CH_3 group of the growing carbonium ion and does not interact with the sterically less accessible protons of the CH_2 groups (Scheme 4).

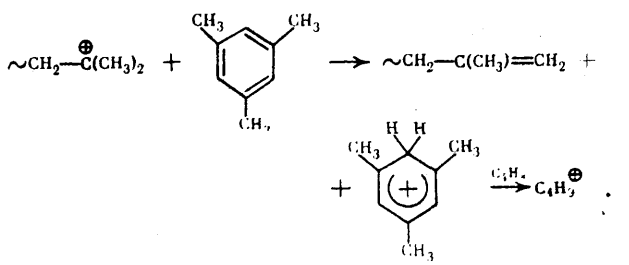
Scheme 4



Apart from its influence on the character of the terminal double bonds, 2,6-di-t-butylpyridine promotes an increase of the molecular weight of the PIB (by an order of magnitude) and a narrowing of its polydispersity (by a factor of 2–3).

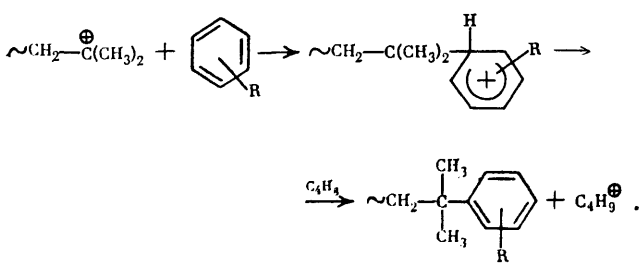
Other sterically hindered aromatic compounds such as 2,4,6-tri-t-butylphenol[19] and 1,3,5-trimethylbenzene[20] can behave in the isobutene polymerisation reaction as mediators in the chain transfer step to the monomer in accordance with Scheme 5 and can broaden the molecular weight distribution.

Scheme 5



In the polymerisation of isobutene in the presence of anisole,[21] 2-alkyl- and 2,4-dialkyl-phenols,[19,22] and certain methylbenzenes,[20] the chain transfer to the monomer is accompanied by the alkylation of the aromatic compounds by the growing carbonium ion with formation of aromatic polyisobutene compounds in accordance with Scheme 6:

Scheme 6



The molecular weight of the functional PIB derivatives is determined by the process temperature and varies from 400 to 200000. The relative contents of the unsaturated and aromatic groups in PIB depends on the ratio of the rates of the competing reactions, which is to a large extent determined by the nature of the catalyst and of the aromatic hydrocarbon (Table 2).

The relative rate constants for the transfer of the polymer chain to methylbenzenes increase with increasing basicity of the aromatic hydrocarbons in the sequence toluene < *m*-xylene < hemimellitol.[20] The presence of aromatic fragments in PIB has been demonstrated by ^1H and ^{13}C NMR and by the EPR of the phenoxy-radicals, obtained on oxidation of the polymers by PbO_2,[19] and by ultraviolet spectroscopy in combination with gel-permeation chromatography.[22] The maximum content of the aromatic end groups in the products has been obtained by polymerisation in the presence of 2,6-dialkylphenols.[19] The contribution of the alkylation reaction increases at lower temperatures and in the presence of the $SnCl_4$ catalyst it becomes dominant.

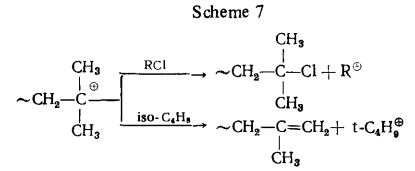
Table 2. Methods of synthesis of polyisobutene with aromatic end fragments at −78 °C.

Catalyst	Reaction conditions		10^{-4} MW*	Relative content of tail groups in PIB, %		Refs.
	aromatic hydrocarbon	solvent		C=C	Ar **	
$(CH_3)_2AlCl$	$C_6H_5CH_3$***	toluene	0.1	90	10	[23]
$C_2H_5AlCl_2$	$C_6H_5CH_3$	toluene	8.5	50	50	[20]
$C_2H_5AlCl_2 \cdot HCl$	$C_6H_5CH_3$	toluene	5.9	40	60	[20]
$C_2H_5AlCl_2 \cdot H_2O$	$C_6H_5CH_3$	toluene	5.1	40	60	[20]
$3C_6H\text{-}CH_3 \cdot 2AlCl_3 \cdot HCl$	$C_6H_5CH_3$	toluene	0.9	20	80	[20]
$AlCl_3(SnCl_4)$	2,6-dimethylphenol	chloroethane	1.1	0	100	[19]
$AlCl_3(SnCl_4)$	2,3,5,6-tetramethylphenol	chloroethane	—	40	60	[19]
$AlCl_3(SnCl_4)$	2,6-di-isopropylphenol	chloroethane	—	—	90	[19]
$AlCl_3(SnCl_4)$	2,6-di-t-butylphenol	chloroethane	0.7	—	99	[19]
$AlCl_3(SnCl_4)$	2-methylphenol	chloroethane	—	—	2.4	[19]
$AlCl_3(SnCl_4)$	phenol		—	—	2.2	[19]
$AlCl_3+SOCl_2$	2-s-butylphenol****	methyl chloride	0.3	—	19.8	[22]
$AlCl_3+SOCl_2$	2-s-butylphenol****	heptane	0.46	—	32.5	[22]

*MW = molecular weight. **Ar = aromatic fragments.
+25 °C. *−70 °C.

Another example of the use of reactions involving chain transfer to a specially introduced reagent in order to obtain a tail functional group other than an unsaturated group (suppression of chain transfer to the monomer) is provided by the polymerisation of IB in the presence of alkyl chlorides. As in the case of aromatic compounds,[20] alkyl chlorides participate in the competitive (relative to the monomer) interaction with the growing centre, leading to the formation of PIB with end fragments in accordance with Scheme 7:

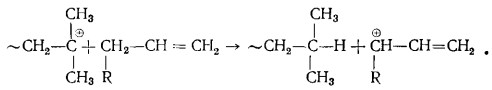
Scheme 7



The ratio of the products[24] is determined by the relative concentrations of RCl and the monomer and by the rate constants for the corresponding reactions. However, the increase in the concentration of RCl entails not only an increase in the chlorine content in the polymer with retention of a high yield of the product[25] but also a significant decrease of its molecular weight. In contrast to RCl (a pure chain transfer agent), α-olefins (chain terminating agents) do not

influence the molecular weight of the product, but significantly reduce the yield (the length of the kinetic chain) as a consequence of the allyl termination reaction[26] with formation of saturated PIB in accordance with Scheme 8:

Scheme 8



Many compounds exhibit both effects to a greater or lesser extent, the effects being quantitatively expressed in terms of empirical poisoning and chain transfer coefficients (Table 3). The knowledge of these quantities provide valuable information about the character of the polymer chain termination reaction under the influence of various additives, which determine the number, size, and nature of the end groups in the PIB molecules formed.

Table 3. Empirical chain transfer and poisoning coefficients in the synthesis of functional derivatives of PIB.[27]*

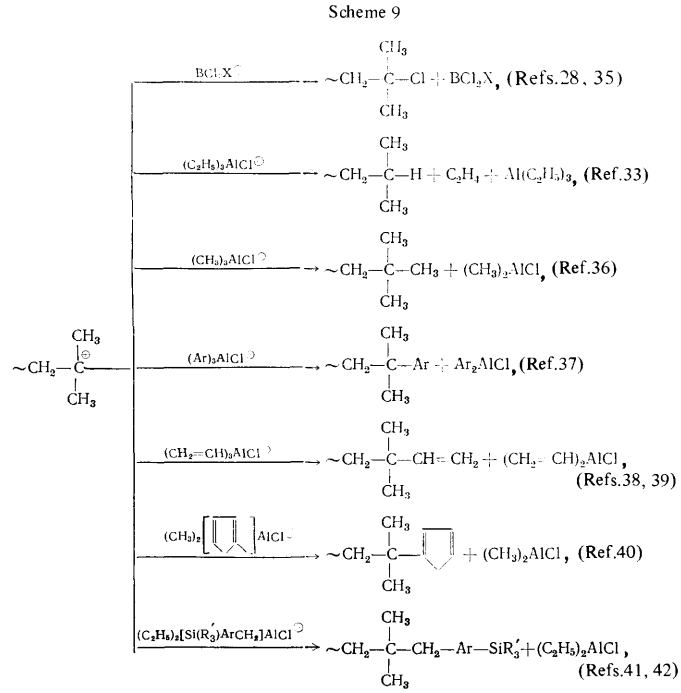
Compound	Coefficients	
	poisoning	chain transfer
Propene	4.9	0
But-1-ene	6.2	0
Pent-1-ene	9.7	0
Hex-1-ene	11.9	0
Oct-2-ene	20.8	12.1
Butadiene	7.6	2.0
2,5-Dimethylhexa-2,4-diene	26.7	15.2
2,3-Dimethylbuta-1,3-diene	107	26
Cyclohexadiene	103	48
Isoprene	140	60
Piperylene	170	327
Cyclopentadiene	900	—
2-Methylcyclopentadiene	685	—
Cyclohexene	5.3	2.7
Cyclo-octone	11	31.2
Cyclopentene	16.3	27
1-Methylcyclohexene	14.7	43.4
1-Methylcycloheptene	66.7	540
1-Methylcyclopentene	280	286
2-Methylpent-1-ene	3.5	53.8
2-Ethylhex-1-ene	24.7	248
2,4,4-Trimethylpent-1-ene	66.7	700
2,4,4-Trimethylpent-2-ene	66.7	34.6
3-Methylbut-1-ene	0	0
4-Methylpent-1-ene	2.9	0
3,3-Dimethylbut-1-ene	0	0
Vinylcyclohexene	3.7	6.7
Indan	10.8	—
Indene	99	210
Norbornene	19.4	57.2
Norbornadiene	16	0
1,5-Cyclo-octadiene	9	1.8
Allyl chloride	0	6.2
Methylallyl chloride	1.6	6.9
2-Chlorobutadiene	6.6	24.5
Crotyl chloride	11.2	27.5
Isopropyl chloride	0	0
Isobutyl chloride	12.5	13.4
t-Butyl chloride	4.4	75.7
Isopropyl bromide	0	0
Isobutyl bromide	1.8	15
t-Butyl bromide	3.5	71.4

*Initiator—$AlCl_3$ in CH_3Cl; solvent—n-pentane; −78 °C.

Wider possibilities, from the standpoint of the preparation of functional PIB derivatives, arise from the chain termination reaction at the initiator fragment. Depending on the nature of the complex initiator $MX_n + R^{\delta+}B^{\delta-}$, one distinguishes termination by a Lewis acid fragment X (for the systems $BCl_3 + H_2O$,[28] $R_2AlCl + RCl$,[28] and $R_2AlCl + Cl_2$ [29]) and termination by the cocatalyst B fragment (for the combination $TiCl_4 + H_2O$, $TiCl_4 + CCl_3COOH$, and $SnCl_4 + C_6H_5OH$ [4,30,31]). The pathways followed in the above polymer chain termination reactions depend on the strength of the donor–acceptor interactions of the components of the initiating system. When it is high ($BF_3 + H_2O$), chain transfer to the monomer with retention of the BF_3OH^- counterion is preferable, as stated above.[12] With decrease in the stability of the complex initiators (based on titanium and tin compounds), the initiation and chain termination proceed with participation of the activated Lewis acid RB, i.e. the cocatalyst behaves as a kind of telogen, forming head and tail groups in the PIB. An additional complexity from the standpoint of the formation of end groups of a specified kind is introduced by systems of the type indicated above, which permit different pathways in the fragmentation of RB, for example, the dissociation of the C–O and O–H bonds in ROH.[32]

Comparison of the experimental and calculated (quantum-chemical analysis of the $\equiv C^+$ or MX_n complex with alcohols by the CNDO/2 method in terms of the Santry–Pople–Segal parametrisation) data shows that the pathway in the fragmentation of ROH bound in a complex depends on the nature of R and the strength of the acid. An increase in the acidity of MX_n and in the degree of branching of the group R promotes the preferential fragmentation of the alcohol at the C–O bond with incorporation of the OH group in the polymer.[32] For $SnCl_4 + C_6H_5OH$,[31] chain termination via the elimination of phenoxy-groups is determined primarily by the effect of the $(p-p)_\pi$ conjugation of the oxygen atom with the aromatic ring, which hinders the rupture of the C(phenyl)–oxygen bond. Since the elimination of the ligands from the MX_nB^- counterion depends on the energy of their binding to the metal and on the stability of the Lewis acid formed, it is possible for the ligand X to be eliminated and then incorporated in the polymer chain in the form of an end group. Reactions of this type occur when relatively weak Lewis acids (BCl_3, R_2AlCl) are used as initiating systems.[28] Numerous model investigations carried out on di- and triisobutenes[33] in the presence of catalysts–cocatalyst systems[34] and also the results of the physicochemical analysis of the polymers established that Cl and R are eliminated from the $[BCl_3R]^-$ and $[R_3AlCl]^-$ counterions respectively in accordance with the scheme:

Scheme 9



where X = OH, Cl, etc., R′ are alkyl radicals, and Ar are fragments of aromatic hydrocarbons.

Because of the absence of chain transfer to IB, the use of these catalysts in absolutely dry systems leads to extensive possibilities not only for the introduction of the specified tail groups into the PIB but also for the synthesis of PIB with functional head groups. The combination of controlled initiation and chain termination methods in the polymerisation of isobutene leads to monofunctional and αω-bifunctional PIB depending on the conditions[37] (Table 4).

Table 4. The synthesis of certain αω-bifunctional PIB.

Initiating system	T, °C	10^{-3}MW of PIB	αω-Bifunctional PIB	Refs.
Cl_2+BCl_3	−40 — −100	—	$Cl-CH_2-C(CH_3)_2-PIB-CH_2-C(CH_3)_2-Cl$	[43]
$CH_2=CH-CH(CH_3)Cl+AlR_3$	−30 — −75	—	$CH_2=CH-CH(CH_3)-PIB-CH=CH_2$	[38]
$(CH_3)_2C=CH-CH_2Cl+BCl_3$	−50	9.3—14.3	$(CH_3)_2C=CH-CH_2-PIB-C(CH_3)_2Cl$	[44]
$Cl-C(CH_3)_2-(CH_2)_3-C(CH_3)_2-Cl+(C_6H_5)_3Al$	−10 — −70	9.0—22.0	$C_6H_5-PIB-C_6H_5$	[45]
$Cl-C(CH_3)_2-C_6H_4-C(CH_3)_2-Cl+BCl_3$	−30 — −70	3.1—100.0	$Cl-C(CH_3)_2-CH_2-PIB-C(CH_3)_2-C_6H_4-C(CH_3)_2-PIB-CH_2-C(CH_3)_2-Cl$	[46, 47]

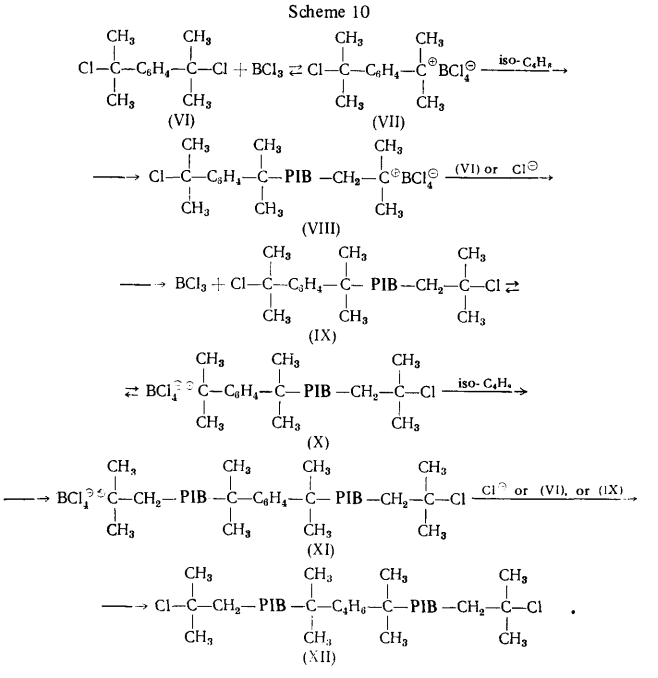
The formation reactions of αω-divinyl-PIB, and α-chloro-ω-vinyl-PIB are based on the principle of controlled chain initiation and termination by the Cl, $CH_2=CH-CH(CH_3)$, and $(CH_3)_2C=CH-CH_2$ cations in the first stage and fragment anions Cl and $CH=CH_2$ in the second respectively. It has been shown[38] that in such cases polymerisation is initiated slowly owing to the greater stability of the primary cationic species compared with the growing PIB carbonium ion. In contrast to the systems indicated, the dihalides combine the functions of the initiator and chain transfer agent. The degree of chain transfer to the monomer in the system is slight, while chain transfer to *p*-bicumenyl chloride is the dominant polymer chain termination reaction.[48,49]

The reactions (Scheme 10) result in the formation of bifunctional PIB containing in the middle of the chain one *p*-phenylene group and two terminal Cl atoms.[46]

The scheme for the formation of αω-dichloro-PIB resembles the cationic telomerisation reaction of isobutene,[50—52] but the products differ by significantly higher molecular weights and have a narrow molecular weight distribution with a width of 1.46—1.70.[47,53]

It is noteworthy that a number of patents deal with the synthesis of PIB having specified end groups. However, owing to the lack of a detailed specification of the experimental conditions, their value is reduced and they are therefore not quoted here.

Scheme 10

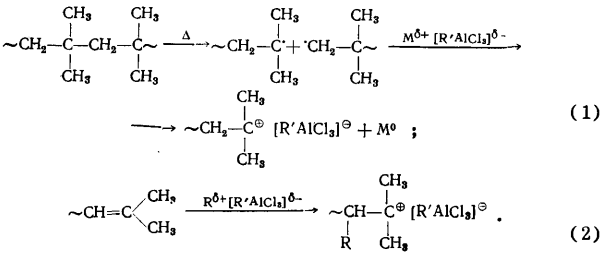


III. DEGRADATION AS A METHOD OF SYNTHESIS OF FUNCTIONAL DERIVATIVES OF ISOBUTENE POLYMERS

The degradation of PIB and PIBC was investigated previously only with the aim of demonstrating the structure (composition) of the compounds[54,55] or to estimate the stability of PIB in relation to various physical influences.[56—58] The free-radical decomposition of PIB proceeds with formation of a complex range of products.[59,60] Furthermore, specific degradation of polymers can serve as a convenient method of synthesis of functional PIB.

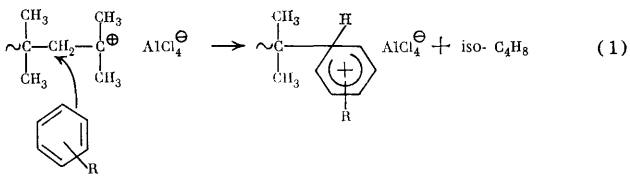
The thermocatalytic degradation of PIB via a mechanism involving depolymerisation under the influence of aluminium chloride complexes has been described.[61—63] Depending on the conditions, it is initiated in accordance with a "random law" via the homolytic dissociation of a C—C bond of the polymer with subsequent redox interaction of the polymer radical and the cation of the complex [Scheme (11), reaction (1)] or in accordance with the "end group" law via the interaction of the complex with the terminal C—C bond of the polymer [reaction (2)]:

Scheme 11

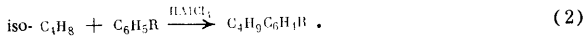


The reaction obeys the general rules for electrophilic processes and in the presence of aromatic hydrocarbons can take place at temperatures below the ceiling temperature for the decomposition of PIB, which is 50 °C.[64-66] The study of the decomposition of PIB in the range from -78° to 200 °C, catalysed by aluminium chloride, showed[64] that the polymer with terminal C=C and C–Cl bonds undergoes degradation from the end of the chain in the presence of ring-alkylating methyl- and isopropyl-benzenes with formation of aromatic polyisobutylene compounds having the general formula $C_4H_9(C_4H_8)_{6-10}C_6H_4$ and t-butyl derivatives of alkylbenzenes. The activating role of the aromatic hydrocarbon in reducing the PIB decomposition temperature below the limiting temperature apparently consists in promoting the fragmentation of the PIB macrocations at the preterminal C–C bond in the coupled alkylation reaction [Scheme 12, reaction (1)] and in binding the IB evolved by alkylating the alkylbenzene with the olefin [reaction (2)]:

Scheme 12



(1)



(2)

When sterically hindered aromatic compounds (mesitylene, tri-isopropylbenzene) are used and also when the reactions are carried out in the absence of alkylbenzenes, the PIB remains indifferent to the action of an acid catalyst under the experimental conditions at temperatures below 50 °C.[64]

More extensive possibilities for the introduction of functional groups into PIB in the degradation process arise from the oxidative cleavage of polymers or copolymers with dienes either at the C=C bonds[67,68] or at the aromatic fragment in the centre of the PIB chain[69] (Table 5).

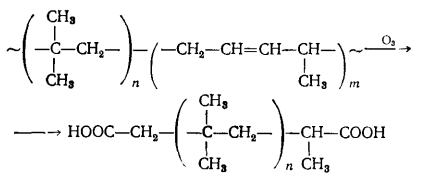
Table 5. The synthesis of αω-bifunctional PIB derivatives by the oxidative cleavage of polymers.

Polymer	Oxidant	Functional derivative	Refs.
$C_6H_{6-n}[C(CH_3)_2-$ PIB $-C(CH_3)_2\cdot Cl]_n$, where n = 2, 3	$CF_3COOH-H_2O_2$	HOOC– PIB –COOH	[69]
Isobutene-piperylene copolymer	O_3 + pyridine	HOOC– PIB –COOH	[67, 70]
Ditto	O_3	OCH– PIB –COOH	[71]
"	RuO_4 + co-oxidant	HOOC– PIB –COOH	[72]
Isobutene-2,3-dimethylbuta-1,3-diene copolymer	RuO_4 + co-oxidant	$CH_3-\overset{\overset{O}{\|}}{C}-$ PIB $-\overset{\overset{O}{\|}}{C}-CH_3$	[72]
Isobutene-isoprene copolymer	O_3	$CH_3-\overset{\overset{O}{\|}}{C}-$ PIB –COOH	[69]

The oxidation of linear and three-arm star PIB having the general formula $C_6H_{6-n}[C(CH_3)_2-PIB-C(CH_3)_2Cl]_n$, where n = 2 or 3, with the $CF_3COOH-H_2O_2$ mixture in the CCl_4-H_2O two-phase system at 60 °C lowers the molecular weight of the polymer by a factor of two (for n = 2) or three (for n = 3) as a result of the cleavage of the aromatic ring and the formation of PIB with terminal ~COOH groups.[69]

When high-molecular-weight PIBC, containing 2–4 wt.% of piperylene, are ozonised in the presence of pyridine, PIB with molecular weights of 1800–4000, containing up to 1.8 COOH groups per macromolecule, are formed[67] in accordance with the scheme:

Scheme 13



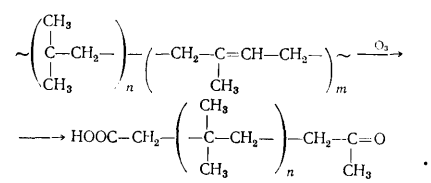
The preparation of these products includes three stages: (1) cleavage of the double bonds with formation of aldehyde and acid groups; (2) oxidation of the aldehydes to acids and peracids; (3) reduction of the peracids to acids.

For the process to be selective, it is necessary to maintain an equimolar ratio of ozone to the diene fragments in the polymer. When this ratio is disturbed, either the degradation of the isobutene chain takes place in the presence of an excess of ozone or the copolymer undergoes incomplete degradation at the diene units if there is insufficient oxidant.[73]

In the controlled ozonisation of PIBC with piperylene in the absence of pyridine, aldehydoacids are formed,[71] while in the presence of pyridine the products are dicarboxylic.[67, 68,70] As a result of a detailed study of the ozonolytic degradation of PIBC with piperylene, the Enjay Company (USA) developed the industrial manufacture of liquid PIB with terminal carboxy-groups.[67] The nature of the terminal functional groups introduced into PIB by this method is determined not only by the ozonolysis conditions but also by the type of the diene fragment in the copolymer.[68]

When isobutene copolymers are ozonised with subsequent thermal decomposition of the ozonides, ketoacids are formed[74] via the scheme

Scheme 14



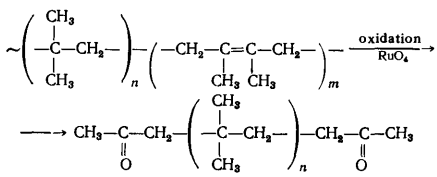
A decrease in the electronegativity of the substituent at the double bond in the copolymer increases its reactivity with respect to ozone (Table 6).

Table 6. The rate constants for the addition of ozone to the double bond in PIBC with dienes.[74]

Copolymer	10^{-5} k, litre mole^{-1} s^{-1}
PIBC with isoprene	10.0
PIBC with penta-1,3-diene	2.9
Brominated PIBC with isoprene	1.0
Chlorinated PIBC with isoprene	0.8

For example, the preparative possibilities of the synthesis of functional PIB derivatives in the course of oxidative degradation are extended when PIBC with 2,3-dimethylbuta-1,3-diene are used. [72] Their oxidation in the presence of catalytic amounts of RuO_4 gives rise to almost quantitative yields of diketones (Scheme 15):

Scheme 15



When the distribution of diene units with the 1,4-configuration in the copolymer is statistical, their content determines the average molecular weight of the degradation products (Table 7). The nature of the diene fragments in the copolymer does not affect the character of the molecular weight distribution of the PIB, which is narrower than in the initial polymer (the M_W/M_n ratio varies from 1.15 to 1.4).

Table 7. The properties of the initial copolymers and the products of their oxidative degradation. [71]

Initial copolymer				Functional PIB derivative	
$10^{-4}\cdot\bar{M}_v$	$\bar{M}_w/\bar{M}_n$	content of diene, mole %	F, wt.%	$\bar{M}_n$	f
Isoprene					
60	—	1.2	20.6	4800	0.81
65	1.8	1.2	20.6	4150	0.9
40	2.84	2.2	17.6	2500	0.92
53	—	6.3	10.3	1080	0.95
Penta-1,3-diene					
38	—	2.3	10.0	2400*	0.97*
38	—	2.3	10.0	2350	1.85
40	—	1.8	—	3500	1.88
35	—	3.6	12.0	1700	1.9
45	2.54	2.0	—	2900*	0.95*
45	2.54	2.0	—	2900	1.9

Notation: $\bar{M}_v$ is the viscosity-average molecular weight, $\bar{M}_w/\bar{M}_n$ the width of the molecular weight distribution, F the content of vinyl units relative to the total number of C=C bonds, and f the functionality with respect to the carboxy-group [number of carboxy-groups per unit].
*Obtained on ozonolysis in the presence of pyridine.

The functionality with respect to the carboxy-group [the number of carboxy-groups per unit] varies from 0.81 to 1.9 as a function of the conditions in the synthesis and the products contain mono-, bi-, and poly-functional derivatives of PIB (Table 8). The presence of "anomalous" fractions with a **functionality** in excess of one (in the case of a ketoacid) or more than two (in the case of a dicarboxylic acid) is due to the deviations from the 1,4-structure of the copolymer [71] in the course of the cationic copolymerisation of the diene with IB. The presence of diene units with 1,2- and 3,4-configurations in the copolymer (Table 7) leads to the formation of formaldehyde and formic acid in the ozonolysis products in accordance with Scheme 16:

Scheme 16

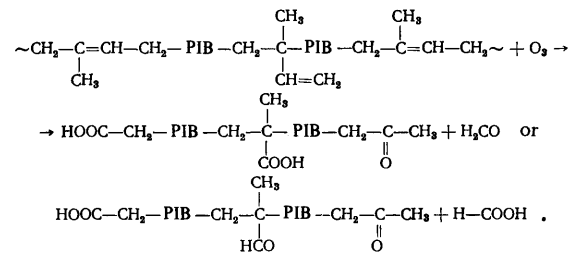


Table 8. Characteristics of carboxyl-containing PIB. [71]

Functional PIB derivative	$\bar{M}_n$	Content of fractions (wt.%) for different functionalities					
		0	1	>1	2	2*	>2
HOOC—PIB —C(=O)—CH$_3$	4800	12.48	70.0	17.5	—	—	—
HOOC—PIB —C(=O)—CH$_3$	2300	6.23	70.63	—	5.87	17.25	—
HOOC—PIB —COOH	2300	6.23	18.3	—	70.85	—	4.62

*Relative to aldehyde groups.

Thus the nature and the number of functional groups in the PIB obtained by the oxidative degradation of the products of the cationic polymerisation and copolymerisation of IB depend to a large extent on the composition and structure of the initial polymers. The development of this method of synthesis of functional derivatives of PIB is therefore associated with the improvement of procedures for the regulation of both the oxidative degradation and copolymerisation processes.

IV. REACTIONS OF ISOBUTENE POLYMERS VIA END GROUPS

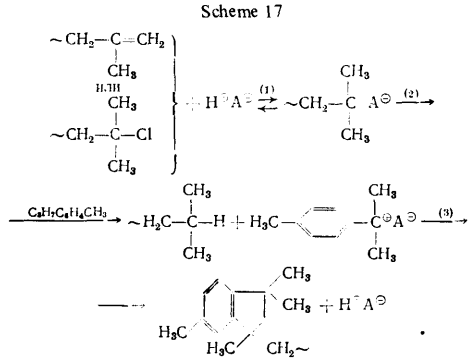
The PIB with one or two reactive end groups obtained in polymerisation or degradation processes are modified by polymer-analogue transformations in order to obtain other functional PIB derivatives (Table 9). These reactions are carried out under conditions which rule out the decomposition and cross-linking of the PIB macrochains. The presence of even one C=C terminal bond in low-molecular-weight PIB makes it possible to introduce into the polymer various groups (chlorine, aromatic groups, etc.).

In contrast to IB, which combines quantitatively with HCl, PIB with a molecular weight of 800 is only partially hydrochlorinated (in solution in toluene the degree of conversion of PIB after 3 h is not more than 50% at 0 °C), while in aliphatic solvents it is totally inactive. [75] With increase in solvent polarity or in the presence of weak Lewis acids ($FeCl_3$, $SnCl_4$, etc.) the degree of conversion of PIB with respect to the end group increases to 86%.

The alkylation of aromatic hydrocarbons (benzene, toluene, [64] and phenol) by PIB with terminal C=C and C–Cl bonds on treatment with acid catalysts leads to the formation of aromatic polyisobutene compounds. In the case of 1-isopropyl-4-methylbenzene, ionic hdyrogenation of PIB takes place under these conditions [77] in accordance with Scheme 17,

which involves the formation of a macrocation [reaction (1)], hydride transfer [reaction (2)], and cycloalkylation of the aromatic ring attached to the second generation carbonium ion [reaction (3)]:

Scheme 17

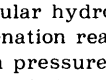
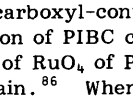


In contrast to catalytic hydrogenation by molecular hydrogen under severe conditions,[78] the ionic hydrogenation reaction takes place at room temperature without high pressure and leads to the formation of PIB with isobutyl and indan groups at the end of the chain in equimolar proportions. The presence of the latter in the products has been demonstrated by ultraviolet spectroscopy and model reactions of di-isobutylene.[79]

The high-molecular-weight alkenylsuccinic anhydride has been obtained in yields up to 58% by the condensation of an unsaturated PIB (molecular weight 800–1000) with maleic anhydride (230 °C, 10 h).[80] Reactions involving hydrosilylation with trichlorosilane and alkylchlorosilanes in the presence of the H_2PtCl_6 catalyst with formation of Si–Cl and (on reduction) Si–H groups are of interest.[51] Various sulphur-containing PIB derivatives can be obtained by the addition of sulphur dichloride, 4-chloro-5-chlorosulphenyl-3-methyltetrahydrophthalic anhydride, or 9-chloro-10-chlorosulphenylstearic acid.[82] PIB chlorination, sulphonation, oxidation, and epoxidation reactions, accompanied not only by the modification of the terminal C=C bonds but also by a change in the chemical nature of the chain are likewise known.[1] Analogous reactions can evidently be achieved with αω-divinyl-PIB obtained by the dehydrochlorination of αω-dichloro-PIB in the presence of $t\text{-}C_4H_9OK$.[83] It has been shown[84] that the epoxidation of PIB containing the vinyl C=C bonds at the end of the chain with the aid of *m*-ClC_6H_4COOOH and subsequent treatment with $ZnBr_2$ lead to a polymeric dialdehyde.

An important intermediate in the synthesis of functional PIB is a carboxyl-containing polymer obtained in the oxidative degradation of PIBC containing dienes[74] or on oxidation in the presence of RuO_4 of PIB with aromatic fragments at the ends of the chain.[86] When αω-dicarboxy-PIB is treated with thionyl chloride, it is readily converted into the corresponding bifunctional acid chloride.[74,86] PIB with carboxy-acid chloride groups have been used for the synthesis of low-molecular-weight polymers with hydroxy-, phenolic, phosphorus-containing, amine, and amidoamine reactive end groups (Table 9). A method of synthesis of dihydroxy-PIB by the hydroboration of αω-divinyl-PIB with subsequent oxidation in an alkaline medium has been described.[85] The product reacts further with isocyanates,[85,89] chlorosilanes,[85] and other reagents. This extends the series of functional PIB. However, one should note that the use of methods for introducing functional groups into high-molecular-weight PIB obtained beforehand is sometimes restricted by the decrease in the reactivity of the end groups with increasing molecular weight of the polymer[79,90] or by the decomposition of the polymer chain under the reaction conditions.[64] These features distinguish the reactions of PIB involving end groups from the reactions of its low-molecular-weight analogues.

Table 9. Modification of PIB via end groups.

Initial groups in PIB*	Reagents	Groups in modified PIB	Refs.
$t\text{-}C_4H_9\sim CH_2\text{—}C(CH_3)=CH_2$	HCl (cat.)	$t\text{-}C_4H_9\sim C(CH_3)_2Cl$	[75]
	C_6H_5R (cat.)	$t\text{-}C_4H_9\sim C_6H_4R$	[64,76,77]
	H_2 (cat.)	$t\text{-}C_4H_9\sim CH_2CH(CH_3)_2$	[78–79]
		$t\text{-}C_4H_9\sim CH{=}CCH_2$	[80]
	$HSiCl_3$	$t\text{-}C_4H_9\sim SiCl_2CH_3$	[81]
	RSCl	$t\text{-}C_4H_9\sim CH_2CH(CH_3)SR$ Cl	[82]
$ClC(CH_3)_2\sim CH_2C(CH_3)_2Cl$	$t\text{-}C_4H_9OK$	$CH_2{=}C(CH_3)\sim CH_2C(CH_3)_2Cl$ CH_3	[83]
$ClCH_2C(CH_3)_2\sim CH_2\text{—}C(CH_3)_2Cl$	MeOH	$ClCH_2C(CH_3)_2\sim CH_2C(CH_3)_2OCH_3$	[87]
$CH_2{=}C(CH_3)\sim CH_2C(CH_3){=}CH_2$	*m*-$ClC_6H_4CO_3H$		[84]
	BH_3; O_2(NaOH)	$HOCH_2CH(CH_3)\sim CH_2CH(CH_3)CH_2OH$	[85]
$t\text{-}C_4H_9\sim C_6H_4R$	RuO_4	$t\text{-}C_4H_9\sim COOH$	[86]
$RC_6H_4\sim C_6H_4R$	RuO_4	$HOOC\sim COOH$	[86]
$HOOC\sim COOH$	$SOCl_2$	$ClOC\sim COCl$	[74,86]
	$LiAlH_4$	$HOCH_2\sim CH_2OH$	[74]
	HOROH	$HOROC(O)\sim C(O)OROH$	[74]
	H_2NRNH_2	$H_2NRNHC(O)\sim\sim C(O)NHRNH_2$	[87]
	$CH_2\text{—}CH\text{—}R$ O	$HOCH_2CHOC(O)\sim$ R $\sim C(O)OCHCH_2OH$ R	[74]
$ClC(O)\sim C(O)Cl$	S $HS\text{—}P(OR)_2$	S $(RO)_2P\cdot C(O)\sim$ S $\sim C(O)\cdot P(RO)_2$	[88]
	ROH	$ROC(O)\sim C(O)OR$	[88]
$HOCH_2\sim CH_2OH$	HOROH	$HOROC(O)\sim C(O)OROH$	[88]
	$ClSi(CH_3)_3$	$(CH_3)_3SiOCH_2\sim\sim CH_2OSi(CH_3)_3$	[85]
	C_6H_5NCO	$C_6H_5NHC(O)O\sim\sim OC(O)NHC_6H_5$	[85]
	$ClC(O)NCO$	$OCNCOO\sim OCONCO$	[89]
	$ZnBr_2$	$OCH\text{—}CH\text{—}CH_2\sim$ CH_3 $\sim CH_2\text{—}CH\text{—}CHO$ CH_3	[84]

*The symbol ~ denotes $-[CH_2\text{—}C(CH_3)_2\text{—}]_n$.

V. APPLICATIONS OF THE FUNCTIONAL DERIVATIVES OF ISOBUTENE POLYMERS

The employment of functional derivatives of PIB in the traditional applications of PIB which have a single double bond at the end of the chain (electrically insulating oils, components of inorganic and synthetic oils, additives to such oils, cooling and lubricating liquids, and ingredients of compound preparations for different purposes[1,91,92]) is of great practical interest. This is because the introduction of functional groups into PIB by the methods described above results in a significant improvement of certain useful properties of the polymer. For example, low-molecular-weight PIB containing heteroatomic fragments at the ends of the chain are characterised by an increased resistance to oxidation compared with unsaturated PIB (octol) (Table 10).

Table 10. Oxidation of functional derivatives of low-molecular-weight PIB at 200 °C and an O_2 pressure of 250 mmHg.[74]

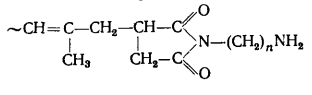
End groups in PIB	Inductive period in oxidation reaction, min
t-C_4H_9~, ~$C(CH_3)=CH_2$, ~$HC=C(CH_3)_2$	0
~COOH, ~$C(O)CH_3$	10
~OH	35
~NH_2	45
~$C(O)SP(O)(OR)_2$	55
~C_6H_4OH	135

The products of the hydrogenation of PIB [79] and aromatic polyisobutene compounds[22,93] exhibit a high resistance to mechano- and thermo-oxidative degradation. The presence of phenolic fragments in the functional PIB derivatives imparts to them the properties of antioxidants.[22]

PIB with terminal carbonyl and carboxy-groups, used as viscosity controlling additives to oils, show a greater thickening capacity than their unsaturated analogues. Functional derivatives of PIB increase the viscosity index without influencing the setting temperature of the petroleum oil and improve its thermal and mechanical stability.[94]

Polyisobutylene with phosphorodithioate end groups (1.5 wt.% of phosphorus and 2.7 wt.% of sulphur) show a polyfunctional activity in lubricating oils, exhibiting not only thickening but also antioxidant, antitear, and antiwear properties. Additives of this type can be regarded as essential materials for creating lubricating oil compositions with improved properties and with a reduced number of components. The high thermo-oxidative stability of these polymers is associated with the formation of phosphorodithioate radicals, which inhibit the decomposition of PIB.[88]

Ashless additives, which are the products of the interaction of polyisobutylenesuccinic anhydride with amines, i.e.



have found extensive applications. A characteristic feature of succinimide additives to motor oils is their effective detergent and dispersing action.[95]

The employment of PIB with carboxy- and keto-end groups as plasticising additives to rubbers makes it possible to improve the frost resistance and the physicomechanical properties of vulcanised chloroprene rubber.[96]

Oils based on aromatic polyisobutylene compounds are distinguished by a low setting temperature.[20] Saturated PIB are also used as lubricating materials in various branches of industry, medicine, and cosmetics.[78]

An advantage of hydrogenated PIB is that, when they are employed as dielectric fluids, the useful life of condensers is 3–4 times longer than in the case where octol (unsaturated PIB) is used as the condenser oil.[79]

High-molecular-weight PIB has a high chemical stability and resistance to ageing but is inadequately compatible with inorganic fillers. Since polymers are used in mixtures with fillers in techniques designed to protect against corrosion and to ensure hermetic seals,[92] the presence of functional groups in PIB is important for the improvement of the compatibility of the mixture components. Functional derivatives of PIB are of greatest interest for the preparation of various gasket and film materials and also compound mixtures, hermetic seals, non-drying putty, adhesive tapes, greases, and dyes, among other general purpose technical materials. By altering the polarity of the macromolecules as a result of the introduction of functional end groups into PIB, it is apparently possible to eliminate also the disadvantage of polyisobutene hermetic seals such as low cohesive strength and instability in relation to oils, fats, lubricants, and many solvents.[92]

Examples of the effective employment of PIB with carboxylic end groups for the modification of polymeric composites based on the acrylonitrile-butadiene-styrene copolymer, which are produced industrially, have been described.[97]

Apart from the traditional applications of PIB, the synthesis of their functional derivatives gives rise to prospects for the creation of liquid rubbers of a new type.[2] The combination of the saturation of the isobutene chain, which imparts a high chemical stability, impermeability to gases, and compatibility with certain polymers to articles based on high-molecular-weight polymers with the advantages arising from the ease of working with liquid rubbers containing highly reactive groups should ensure a wide variety of applications of these compounds. The hardening of oligoisobutenedicarboxylic acid by epoxy-compounds in the presence of tertiary amines as catalysts is accompanied by the formation of rubbers with a regular three-dimensional network.[90]

The presence of the reactive acid chloride group in PIB permits the subsequent grafting of starch via the CH_2OH groups[98] and also the preparation of a PIB block copolymer with polystyrene by reaction with the "living" polymer.[86]

Depending on the number and nature of the reactive groups, functional derivatives of PIB can be used as prepolymers in the synthesis of block copolymer of the type PIB-A, A-PIB-A, and $(PIB)_nA_m$, where A are blocks of a polymer differing in its nature from PIB. For example, the diblock (PIB–PST) and triblock (PST–PIB–PST) copolymers have been obtained by initiating the cationic polymerisation of styrene with alkyl derivatives under the influence of the PIB-Cl + alkylaluminium halide macromolecular initiator.[99]

Monofunctional PIB with a terminal chlorine atom attached to a teritary carbon atom reacts to form an IB block copolymer with styrene having a molecular weight up to 80000–100000 with a conversion up to 98% after the addition of $Al(C_2H_5)_2Cl$ and styrene.[100] Functional derivatives of diblock copolymers of isobutene with styrene or α-methylstyrene have been synthesised by an analogous procedure. PIB with a molecular weight from 9300 to 14300, having a tertiary Cl atom at one end of the chain and the $(CH_3)_2C=CH-CH_2$~ or $CH_2=CH-C(CH_3)_2$~ group at the other, was used as the prepolymer.[37] It has been shown[101] that chain transfer to α-methylstyrene with formation of a homopolymer does not occur in this instance and the product is characterised by a unimodal molecular weight distribution.

The reaction of bifunctional PIB having terminal chlorine atoms (whose molecular weights are in the range 30000–100000) with α-methylstyrene in the presence of $(C_2H_5)_2AlCl$ leads to a triblock copolymer consisting of a central PIB block and two terminal poly-α-methylstyrene blocks.[48]

The polymeric Grignard reagent synthesised on the basis of αω-dichloro-PIB has been used to prepare a new poly(isobutene–block–methyl methacrylate) block copolymer[43] in accordance with the scheme

Scheme 18

$$\mathrm{ClCH_2{-}C(CH_3)_2{-}\,PIB{-}CH_2{-}C(CH_3)_2Cl} \xrightarrow[2)\ Mg\ (THF)]{1)\ CH_3OH(HCl)} \longrightarrow$$
$$\longrightarrow \mathrm{ClMg{-}CH_2{-}C(CH_3)_2{-}PIB{-}CH_2{-}C(CH_3){=}CH_2} \xrightarrow{MMA} \longrightarrow \sim \mathrm{PMMA{-}CH_2{-}C(CH_3)_2{-}\,PIB{-}CH_2{-}C(CH_3)_2{=}CH_2}\ ,$$

where MMA is methyl methacrylate and PMMA is poly(methyl methacrylate).

By virtue of the presence of polystyrene, poly-α-methylstyrene, poly(methyl methacrylate), and other blocks in the products, they have the properties of thermoelastoplastics.[43] This leads to promising new applications of isobutene polymers.

The methods for the introduction of functional end groups into PIB reflects the characteristic features of the synthesis and properties of the polymer. The inapplicability to PIB of the method for the introduction of functional groups traditional for polymers based on anion-active monomers and based on the principle of "living polymerisation" as well as the limited possibility for polymer-analogue transformations via the terminal double bond have given rise to the use of new procedures. These include the cationic polymerisation of IB, regulated at the level of elementary chain intitiation and termination (transfer) stages, using specially selected complex catalysts, weak electron-donating compounds (chain transfer agents), proton traps, etc., which makes it possible to synthesise PIB with specified functional groups at the end of the chain. The picturesque term "molecular engineering" given to this method for the introduction of functional groups into PIB [102] neatly reflects the high level of the solution of the problem: together with the specified functionality and the distribution of functional groups, a specific molecular weight, molecular weight distribution, and microstructure of the polymer are ensured. In other words, one is dealing with the synthesis of functional derivatives of PIB regulated at different levels.

By means of further development of research into the controlled cationic polymerisation of IB in the absence of protic initiation and chain transfer to the monomer, it is possible to approach and even surpass the synthetic possibilities of "living" systems as regards the preparation of a wide variety of block and grafted copolymers.[102]

The synthesis of cationic copolymers (susceptible to regulation) of IB with diene (1,4-addition) and triene (1,6-addition) monomers and subsequent oxidative degradation under specially selected conditions also lead to extensive possibilities for the synthesis of functional PIB derivatives. Despite the large number of stages involved and their complexity, the oxidative degradation methods can compete successfully with polymerisation procedures for the synthesis of functional PIB derivatives, particularly in the synthesis of high-molecular-weight dihydric alcohols and dicarboxylic acids. The range of chemical reactions and applications of PIB as hermetic seals, oils, additives, etc. can be significantly extended by modifying the polymer at the end groups. The presence of reactive groups in functional PIB derivatives makes it possible to combine this polymer chemically with "incompatible" plastics and elastomers to form polymeric products with a unique set of properties.

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