Polyisoprene synthesized via cationic polymerization: State of the art*

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Abstract: In this paper, more than 70 years of cationic polymerization of isoprene (IP) are reviewed. Up to now, the controlled or living cationic polymerization of IP was never reported due to numerous side reactions, including chain transfer, cyclization, and cross-linking reactions that were very difficult to control. Cationic polyisoprenes (PIPs) are thus described to be mainly 1,4-*trans* with saturated/cyclized sequences. Although progress was made for their characterization due to many analysis techniques, cationic PIPs are still not yet fully characterized, particularly the saturated sequences. As a consequence, even if suggestions are proposed, polymerization mechanism is still not fully elucidated.

Keywords: cationic polymerization; infrared; isoprene; Lewis acids; NMR.

INTRODUCTION

Polyisoprenes (PIPs) can be produced by a large number of plants as well as by distinct synthetic routes. These various natural or synthetic rubbers of different structures could exhibit very different properties. Although natural PIPs result from the polycondensation of isopentenyl pyrophosphate, synthetic PIPs are obtained from isoprene (IP), a monomer that presents the not-so-common feature to be polymerizable through all types of polymerization mechanisms, i.e., anionic [1,2], free-radical [3–6], coordination [7–10], and cationic, leading to PIPs with different microstructures (Scheme 1).
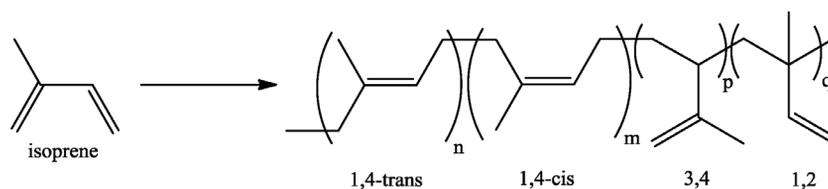
Scheme 1 Microstructures of PIP.

IP cationic polymerization, even if not as active as other cationically polymerizable monomers (vinyl ethers, isobutene, etc.) [11,12], has been studied for more than 70 years. As will be shown, a broad variety of cationic polymerization systems were investigated and most of the time, ill-defined PIPs containing unusual microstructures, such as cyclized sequences, were described. Until the beginning of the 1970s, structural characterization was mainly performed by infrared (IR) or Raman spectroscopy by comparison with known and well-defined structures and by titration. Since then, many

other techniques have been used. Nevertheless, the cationic PIP microstructure remains still partially unknown. In particular, one main feature of cationic PIPs is the loss of double bonds (DBs) during the polymerization that leads to saturated sequences that are up to now not identified.

CATIONIC POLYMERIZATION OF ISOPRENE

The cationic polymerization of IP was studied in the presence of a large number of catalytic systems [13–41]. Up to the end of the 1960s, Friedel–Crafts catalysts, Lewis acids, and/or other organometallic compounds were mainly used as initiating systems, while the use of protic promoters started in the 1970s. Some illustrative examples are listed in Table 1. Many polymerization conditions were examined including variation of the solvent, the temperature, the monomer, and catalytic systems concentrations.

Table 1 Cationic polymerization of IP.

Catalytic systems	Solvents	ε	T(°C)	References
BF_3	Pentane	1.84	30	[13]
$BF_3 \cdot Et_2O$	Dichloromethane	8.93	0	[29]
$BF_3 \cdot H_2O$	Hexane	1.88	5	[33]
$SnCl_4$	Chloroform	4.81	–45 to 30	[13]
$AlCl_3$	Ethylbromide, heptane, benzene	9.5;1.92;2.27	–78 to 30	[13,17,18,22,34]
$AlEtCl_2$	Heptane, benzene, nitrobenzene	1.92;2.27;1.56	–20 to 20	[14,17,18,22,27]
$AlEtCl_2/TiCl_4$	Heptane, benzene	1.92;2.27	–78 to 80	[17,19–21,24]
$RMgBr/TiCl_4$	Benzene	2.27	20	[16]
$TiCl_4$	Heptane	1.92	20	[17,22]
$C_7H_7{}^+SbCl_6{}^-$	Nitrobenzene	1.56	20	[23]
$Ph_3C^+SbCl_6{}^-$	Nitrobenzene	1.56	20	[23]
H_2SO_4	Dichloromethane	8.93	25	[26]
$^tBuCl/TiCl_4$	Dichloromethane	8.93	25	[26,28]
$CCl_3COOH/TiCl_4$	Dichloromethane, benzene	8.93;2.27	25	[28,30,35,38]
$CumylOMe/TiCl_4$	Methyl chloride/n-hexane	9.1;1.88	–40	[31]
DMAX/Lewis acid	Dichloromethane, cyclohexane	8.93;2.02	–60 to 20	[39,40]
$MeOPhEtOH/B(C_6F_5)_3$	Dichloromethane, water	8.93;80.1	–30 to 20	[41]

The polymerization yield is highly dependent on the catalytic system used. For instance, Richardson showed that 50 % conversion was reached after several days, hours, or minutes with BF_3/pentane/30 °C, $SnCl_4$/chloroform/–45 to 30 °C, or $AlCl_3$/EtBr/–78 °C, respectively [13]. One of the main features observed by all the authors was the two-stage polymerization rate: a first stage of rapid and linear IP consumption followed by a second stage of moderate to very low activity [14,17,18,20,41]. The initial polymerization rate was generally dependent on monomer and catalyst concentrations [14,17,30,35,41], as well as on the ratio between the components of the catalytic system. For instance, the polymerization yield was highly dependent on the $PhMgBr/TiCl_4$ ratio [16]. Indeed, as $TiCl_4$ alone was not able to initiate the IP polymerization (unless adventitious water was present), following the conversion vs. $PhMgBr/TiCl_4$ ratio, 2 maxima were observed at ratios of 1 and 4, leading to polymers with very different aspects. For the $AlEtCl_2/TiCl_4$ catalytic system, it was shown that the ratio between the 2 components leading to the highest yields was <1 [17]. Besides, some authors demonstrated that catalyst aging was also very important and dependent on the components ratio [17,20]. Indeed, it is described that the polymerization yield is dependent on the latency period for the formation of the active species before the monomer addition.

The nature of the solvent may also have a great effect on the polymerization yield. As it could be noticed, polymerization rates are highly dependent on the dielectric constant. Furthermore, in aliphatic solvents (hexane, heptane), yields are generally lower than in aromatic [18,20,21,24,27] and chlorinated

solvents [18]. For instance, polymerization performed with $AlEtCl_2$ alone in heptane was almost stopped after low conversion, but could be reactivated with high rate by adding new monomer to be almost stopped again after low conversion [25,27]. Nevertheless, after several weeks a quantitative conversion was achieved. With stable carbenium as initiating species like $C_7H_7^+SbCl_6^-$ or $Ph_3C^+SbCl_6^-$, the influence of the solvent was even more pronounced. In heptane, benzene, toluene, and acetonitrile, no polymerization occurred; in dichloromethane or nitromethane, only traces of polymer were detected; whereas in nitrobenzene, conversion reached around 40–50 % with $Ph_3C^+SbCl_6^-$ and a bit less with $C_7H_7^+SbCl_6^-$ [23].

POLYISOPRENE CHARACTERIZATION

During the first studies on cationic IP polymerization, characterization of the resulting polymers was quite difficult. The amount of DBs was nevertheless estimated by titration techniques and the polymer microstructure could be evaluated by IR or Raman spectroscopies. The development of NMR allowed a better characterization even if, as will be described, up to now cationic PIPs are not fully characterized due to very complicated microstructures. Indeed, depending on the polymerization conditions (catalytic system, solvent, temperature, etc.), tacky to crumbly solids or soluble to insoluble polymers were obtained.

Polyisoprene double bond content

One common feature of all cationic PIPs is the loss of DBs as indicated in Table 2. For the determination of residual unsaturations, various methods were used. Up to the 1970s, DB content was mainly evaluated by IR spectroscopy [14,16,20,22,23,26] and titration with iodine monochloride (ICl) [18,20,21,26,27]. Afterwards, NMR became the technique employed for all studies [26,29,33,34,36,40,41]. It was mentioned that the DB content evaluated by NMR was generally higher than that estimated with ICl titration [26]. As will be discussed later on, the loss of DB is attributed to cyclization, branching, or cross-linking reactions leading to saturated units or sequences. Nevertheless, some authors mentioned that the cyclized sequences may still contain some DBs [21,26]. Very recently, Kostjuk et al. showed that fully unsaturated PIPs could be obtained in water [41].

Table 2 DB content of cationic PIPs prepared in different conditions.

Catalytic systems	Solvents	Remaining DB (%)	References
$AlEtCl_2/TiCl_4$	Heptane, benzene	<15	[17,20,24]
$C_7H_7^+SbCl_6^-$	Nitrobenzene	~25	[23]
$AlEtCl_2$	Heptane, benzene, nitrobenzene	<30	[18,22,27]
$RMgBr/TiCl_4$	Benzene	<30	[16]
$Ph_3C^+SbCl_6^-$	Nitrobenzene	10–35	[23]
$BF_3 \cdot Et_2O$	Dichloromethane	25–35	[29]
$BF_3 \cdot H_2O$	Hexane	~50	[33]
$AlCl_3$	Ethylbromide, heptane, benzene	60	[13]
$^tBuCl/TiCl_4$	Dichloromethane	30–60	[26]
BF_3	Pentane	50–75	[13]
DMAX/Lewis acid	Dichloromethane, cyclohexane	40–80	[40]
$MeOPhEtOH/B(C_6F_5)_3$	Dichloromethane	60–80	[41]
$SnCl_4$	Chloroform	~80	[13]
$CCl_3COOH/TiCl_4$	Dichloromethane, benzene	55–90	[36]
$MeOPhEtOH/B(C_6F_5)_3$	Water	>95	[41]

Infrared and Raman spectroscopy

At the early stage of cationic IP polymerization studies, the microstructure was usually determined using IR and Raman spectroscopies, by comparison with PIPs of known structures [42–51] or with intentionally cyclized synthetic or natural rubbers [52,53]. Saunders et al. [51] and Sutherland et al. [54] were among the first to discuss the IR spectra and structure of the hevea and gutta elastomers and concluded that these two polymers corresponded to *cis-* and *trans-*PIPs, respectively. Some years later, Binder did spectral analysis of different PIPs and proposed some modifications to the previously suggested assignments. The main bands of PIPs with their vibration frequencies are summarized in Table 3. Although IR assignments were not fully complete, all cationic PIP characterizations were based on these investigations. It must be mentioned that 1,4-units have low band absorptions that can shift slightly depending on the overall structure of the polymer, which renders their quantification difficult (error of at least 5–10 %). Since those studies, most authors used series of band for the detection of the different units. For instance, 1,4-*cis* units are generally identified by specific bands at 572, 742 and 762, 1130, and 1315 cm^{-1}; 1,4-*trans* units by specific bands at 600, 800, 1150, and 1335 cm^{-1} and 3,4-units by specific bands at 888, 1140, 1378, and 1780 cm^{-1}. Some other bands are characteristic of 1,4-units (either *cis* or *trans*): 840, 980, and 1665 cm^{-1}. Nevertheless, according to some authors, quantification of 1,4-, 3,4-, and 1,2-units were usually based on bands at 840, 888 (isoprenyl group), and 910 cm^{-1} (vinyl group), respectively, since those are strong bands [42,45,52,55].

Table 3 Main IR characteristic bands reported for cationic PIPs [44,51,54].

cm^{-1}	Assignments
3077	=CH stretch ($-CCH_3=CH_2$)
3000	=CH stretch ($-CCH_3=CH-$)
2924	CH_3 stretching antisymmetrical
2907	CH_3 in plane stretching
2890	CH_3 stretching symmetrical
2833	CH_3 out-of-plane stretching
1665	C=C ($-CCH_3=CH-$)
1645	C=C ($-CCH_3=CH_2$)
1450	CH_3 antisymmetrical
1380	CH_3 symmetrical
1361	CH_2 wag
1325	=CH (*trans* $-CCH_3=CH$)
1315	=CH (*cis* $-CCH_3=CH$)
1245	CH_2 twist
1152	$C-CH_3$ (*trans* $-CCH_3=CH$)
1130	$C-CH_3$ (*cis* $-CCH_3=CH$)
1105	$C-CH_2$ stretching
1040	CH_3 rock
1013	$C-CH_2$ stretching
980	$C-CH_3$ stretching
890	CH out-of-plane bending ($-CCH_3=CH_2$)
878	CH_3 wag out-of-plane
845	CH wag out-of-plane (*trans* $-CCH_3=CH$)
840	CH wag out-of-plane (*cis* $-CCH_3=CH$)
762	$CCH_3=CH$
742	$CCH_3=CH$

As mentioned above, in order to know more about the microstructures of cationic PIPs and especially on that of the saturated sequences, natural and synthetic PIPs of different unit configuration were subjected to cyclization reactions and their structure compared to PIP obtained by direct IP cationic polymerization. To this end, different catalysts (such as sulfonic acids and sulfonyl chlorides [56], $TiCl_4$ [57–59], $SbCl_5$ and $SnCl_4$ [59], HCl [60,61], H_2SO_4 [62–64], *p*-toluenesulfonic acid [57,65], trimethylsilyl triflate [66]) were used. The obtained resinous products exhibited the same empirical composition, $(C_5H_8)_n$, as PIP.

When NR was cyclized, the main changes were a decrease of the intensity of the bands at 572 cm^{-1} (until extinction at high cyclization degree), 838, 2750, and 3040 cm^{-1}, which was accompanied by a shift of bands at 1455 and 1665 cm^{-1} to 1465 and 1670 cm^{-1}, respectively. In the same time, new bands appeared at 885, 696, and 732 cm^{-1} and then disappeared at high cyclization degree to the benefit of a strong band at 1175 cm^{-1} attributed to terminal DBs. Fully cyclized natural rubber exhibited a spectrum with main bands at 810, 885, 1040, 1265, and a low intensity band at 1200 cm^{-1}. Cyclization of Balata leads to an intensity decrease of the bands at 789, 878, and 3049 cm^{-1} and a shift of the bands at 845, 1384, and 1455 cm^{-1} to 810, 1378, and 1465 cm^{-1}, respectively. Cyclization of 3,4-PIP was characterized by a shift of the bands at 566 and 1085 cm^{-1} to 580–590 and 1100 cm^{-1}, respectively, a splitting of the band at 1378 cm^{-1} into two bands at 1370 and 1385 cm^{-1} and an intensity decrease of the band at 3077 cm^{-1}. Moreover, new bands at 618, 1015, 1050, and 1265 cm^{-1} were observed. On the whole, no significant difference was observed between the IR spectra of cyclized natural rubber, Balata, and 3,4-PIPs. They all exhibited the same new absorption bands at 3060, 2070, and 1265 cm^{-1}, weak bands at 810, 1040, and 1200 cm^{-1} and a strong band at 1175 cm^{-1}. The major change in cyclized 3,4-PIP was the presence of two bands at 1370 and 1385 cm^{-1} and small ones at 725 and 760 cm^{-1} [44,63]. Main bands of cyclized PIPs are summarized in Table 4.

On the basis of PIP cyclization studies, it seems difficult to identify the exact structure of the cyclized units (mono-, bi-, or polycyclic), as it varies with the cyclization extent indicated by the appearance and disappearance of bands. Based on 50 % loss of DBs, Gordon and D'Ianni proposed the formation of monocycles [62,67,68], whereas Golub and Heller suggested first the formation of bicyclic structures and later on, comparing IR and NMR analysis of cyclized 1,4-*cis*-PIP, they privileged the formation of tricyclic structures [58,69]. Tutorskii suggested a cyclicity of 2–3 [70], whereas many other authors proposed polycyclic structure [71–73]. The debate is still open. From the most recent studies, it was concluded that the cyclized sequences contain both mobile and rigid domains due to cross-linking during the cyclization reaction, showing three types of olefinic-segmented end-groups (di-, tri-, and tetra-substituted olefins). Sakdapipanich assigned a weak band at 1692 cm^{-1} to the C–C stretching of the tetra-substituted endocyclic unit in the cyclized sequence and a band at 884 cm^{-1} to the C–H bending of the exocyclic fragment [64]. The C–H out-of-plane deformation of the original 1,4-*cis* IP units was observed at 836 cm^{-1}. A band at the low-frequency side of the 836 cm^{-1} band shifted from 820 to 815 cm^{-1}.

One difficulty arising with IR measurements is that characteristic bands of each type of units are affected by their neighbor units and values are generally given for long sequences (natural rubber, Balata, etc.). Under cyclization, sequences of the same units became shorter and band frequencies are then shifted. As a consequence, some bands are superimposed and their assignments become very difficult. For example, pure 1,4-*trans* units are characterized by a band at 1150 cm^{-1}, pure 1,4-*cis* units are characterized by a band at 1130 cm^{-1}, but in different environments, both bands shift to 1140 cm^{-1}, which is also the characteristic band of 3,4-units. IR spectroscopy appears then not to be very adapted to the characterization of such complex molecules.

Table 4 Main IR characteristic bands of cyclized PIPs [52].

Absorption bands for C–H and C–C vibrations in cyclic segments	
cm^{-1}	Assignments
2950	C–H stretching of –CH$_3$ antisymmetrical
2920	C–H stretching of –CH$_2$ antisymmetrical
2900	C–H stretching of –CH
2865	C–H stretching of –CH$_3$ symmetrical
2850	C–H stretching of –CH$_2$ symmetrical
1465	C–H deformation of –CH$_2$ and of –CH$_3$ antisymmetrical
1382	C–H deformation –CH$_3$ symmetrical
985	C–C stretching of C–CH$_2$ in ring

Absorption bands for typical end-groups in cyclic segments	
cm^{-1}	Assignments
3070	CH$_2$ stretching of =CH$_2$ (exomethylene)
1670	C=C stretching of R$_1$R$_2$C=CR$_3$R$_4$
1665	C=C stretching of R$_1$R$_2$C=CR$_3$H
1650	C=C stretching of C=CH$_2$
1440	C–H in-plane deformation C=CH$_2$
1370&1385	Doublet of C–H deformation of two –CH$_3$ on the same carbon
1330–1350	*Not assigned*
1265	*Not assigned*
1160	C–C stretching in =C–CH$_2$ in ring
1100	C–C stretching in =C–CH$_3$ in ring
1040	–CH stretching in =C–CH$_3$
985	*Not assigned*
910	Out-of-plane =CH$_2$ in CH$_2$=CH–
890	Out-of-plane =CH$_2$ in CH$_2$=CR$_1$R$_2$
850–860	Out-of-plane =CH$_2$ in C(CH$_3$)=CH
810	*Not assigned*

Raman spectra of different PIPs were also obtained, and the frequencies were assigned by Cornell et al. [74]. More recently, the IR and Raman spectral analyses of 1,4-*trans*-PIP were carried out by Mohan and colleagues, who provided some effective information on its fundamental vibrations [50]. Raman analysis showed that during the cyclization, the absorption band at 1664 cm^{-1} assigned to the C=C stretching modes clearly decreased with no alteration of the band at 1452 cm^{-1} assigned to an anti-symmetric vibration of the –CH$_3$ group. The main bands of PIPs with their vibration frequencies are summarized in Table 5.

Based on all these analyses, the microstructure of the unsaturated units of cationic PIPs were found to be mainly 1,4-*trans* units with some traces of 3,4- and 1,2-units as indicated in Table 6. Results obtained using AlEtCl$_2$/TiCl$_4$ indicated that mainly 1,4-*cis* addition was obtained, which was quite unusual for cationic polymerization. Nevertheless, as will be discussed later in the paper, the proposed mechanism was not fully cationic. Moreover, the amount of residual DBs was only 10–15 %. Concerning the saturated units, even if their amount is always large in cationic PIPs, little information could be deduced from IR.

Table 5 Main characteristic Raman bands for cationic PIPs [50,74].

1,4-*cis*	1,4-*trans*	3,4-	1,2-	Assignments
1662	1669	1641	1643	C=C stretching
1445		1442	1440	CH_3 deformation
1431	1444	1431		CH_2 deformation
	1384		1372	CH_3 antisymmetric deformation
1359	1365		1354	CH_3 symmetric deformation
1321	1330	1304	1304	CH_2 wagging
1130	1154			CH_3 wagging
1038	1048			CH_3 rocking
889	882	885		=C–H out-of-plane bending
565	600			C–C in-plane bending
	455			C–C out-of-plane bending

Table 6 Examples of microstructures of cationic PIPs evaluated by IR or NMR.

Catalytic systems	1,2 (%)	3,4 (%)	1,4-*cis* (%)	1,4-*trans* (%)	References
BF_3	3–4	6–7	0	90	[13]
$BF_3 \cdot Et_2O$	0	0	0	100	[29]
$SnCl_4$	4–6	4–5	0	89–92	[13]
$AlCl_3$	3	4	0	93	[13]
$AlEtCl_2$	7	14	79		[18,27]
$AlEtCl_2/TiCl_4$	0	10–40	60–90	0	[17]
$C_7H_7^+SbCl_6^-$	0	<5	0	>95	[23]
$Ph_3C^+SbCl_6^-$	0	<5	0	>95	[23]
$^tBuCl/TiCl_4$	1–4		0	96–99	[26]
$CCl_3COOH/TiCl_4$	5	6	0	89	[36]

NMR spectroscopy

Characterization of cationic PIPs became easier with the development of NMR analysis. Along time, several peak assignments were achieved with more and more accuracy [37,39,40,75–81]. The analysis of PIPs synthesized via other mechanisms was also very helpful for peak assignments [3–5,82]. As already determined by IR, cationic PIPs are mainly composed of 1,4-*trans* repeating units, whereas the 1,2- and 3,4-isomers are present as minor components.

Both ^{1}H and ^{13}C NMR spectroscopies allow the determination of all IP unit types (1,4-, 3,4-, and 1,2-). However, since the olefinic and methylenic protons of 1,4-*cis*- and 1,4-*trans*-units exhibit similar or very close chemical shifts, their distinction using ^{1}H NMR is difficult and can rely on the methylene proton peak shape; a *cis* unit exhibits a singlet while a *trans*-unit appears as a broad doublet. When 1,4-addition is predominantly *trans*, which is the case with cationic PIPs, traces of *cis* DBs become undetectable. ^{13}C NMR is more accurate and allows characterization of *cis*-units via specific signals of their methyl and methylene groups at 23.4 and 32.2 ppm, whereas the corresponding peaks in *trans*-units are located at 16 and between 28.5–39.7 ppm (depending on adjacent units), respectively. The different type of sequences of 1,4-*trans*-units, i.e., *head to tail*, *head to head*, and *tail to tail*, were also assigned by Rozentsvet using ^{13}C NMR. Results are collected in Table 7.

Table 7 ^{1}H and ^{13}C NMR signals of cationic PIPs according to Tanaka and Rozentsvet (nd: not determined) [37,39–41,76,78,83].

Units			NMR assignments				
			1, 1'	2, 2'	3, 3'	4, 4'	5, 5'
1,4-*cis*		[1]H	2.01		5.10	2.01	1.68
		[13]C	32.2	134.8	125.0	26.4	23.4
1,4-*trans*	"head to tail"	[1]H	1.99–2.05		5.05–5.40	1.99–2.05	1.60
		[13]C	39.7	134.9–135.3	124.2	26.7	16.0
	"tail to tail"	[1]H	nd		5.05–5.40	2.00–2.04	1.60
		[13]C	nd	134.9–135.3	124.2	28.3	16.0
	"head to head"	[1]H	2.00–2.04		5.05–5.40	nd	1.60
		[13]C	38.5	134.9–135.3	124.2	nd	16.0
1,2-		[1]H	1.25		5.70–5.87	4.80–5.05	0.95
		[13]C	nd	40.4	147.7	111.1	22.1
3,4-		[1]H	1.90	2.25		4.60–4.80	1.60
		[13]C	22.9	44.9	147.7	111.1	18.8
DMA head		[1]H	1.70		5.08	nd	1.60
		[13]C	25.8	131.3	124.9	nd	17.7

^{1}H and ^{13}C NMR spectroscopies also allow identification of the main-chain termini. For example, dimethylallyl (DMA) chain ends, characterized by a proton signal at 5.1 ppm, are attributed to protic initiation, signals at 4.6–4.7 ppm correspond to unsaturated chain ends resulting from proton elimination, whereas the signal at ~4.1 ppm indicates termination of PIP allylic ends by a hydroxyl group [37,41]. ^{1}H NMR also shows the formation of saturated units characterized by a broad signal at 0.85–1.0 ppm and allows the evaluation of DB loss during cationic IP polymerization through integration of olefinic protons with regards to aliphatic protons.

The microstructure of cyclized PIPs, i.e., PIPs submitted to a post-polymerization cationic reaction using various catalytic systems, was also investigated by ^{1}H and ^{13}C NMR spectroscopies. Three types of terminal alkene sequences (di-, tri-, and tetra-substituted) were assigned on the basis of ^{1}H NMR in agreement with IR data [84] (Fig. 1). In most cases, tetra-substituted alkenes predominated. A singlet centered at 5.16 ppm was assigned to the remaining olefinic protons, a signal centered at 2.10 ppm was attributed to methylene protons, and a singlet centered at 1.70 ppm to methyl protons. Riyajan et al. showed that the intensity of the signal at 5.16 ppm decreased with time during the cycliza-
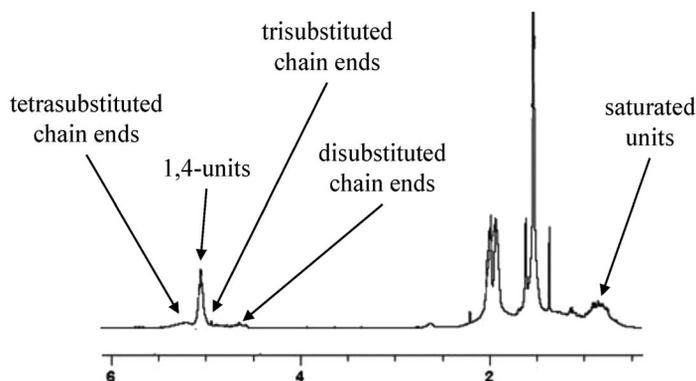
Fig. 1 ^{1}H NMR spectrum of partially cyclized PIP.

tion process, while the intensity of a signal at 0.86–1.00 ppm increased [64,66]. The latter could be attributed to methyl protons attached to a saturated carbon in ring structure, which were resolved as a triplet centered at 0.85 ppm in small ring hydrocarbon molecules [57]. Another new signal centered at 1.3 ppm was assigned to methylenic protons attached to a saturated carbon. These signals increased in intensity while the methylene proton of original linear IP units centered at 2.05 ppm decreased. Furthermore, new signals at 5.32 and 4.64 ppm were attributed by Sakdapipanich to olefinic endo- and exo-six-membered cycles, respectively [57,64,66]. Thus, on this basis, ^{1}H NMR analysis enables a quantification of unsaturated/saturated units and a full characterization of the unsaturated units. Further characterization of the structure of saturated units is difficult since it relies only on a broad and unresolved signal centered at 0.85 ppm attributed to cyclized IP sequences. No peaks corresponding to saturated units could be detected by ^{13}C NMR, preventing further characterization (cycles and/or branching point).

Other techniques

Molar mass analysis

As already mentioned, depending on the polymerization conditions, soluble and/or insoluble PIPs were produced. Before the possibility to evaluate molar masses by light scattering (LS) or size exclusion chromatography (SEC), viscosity measurements were made and were related to chain length [23,24,28]. LS measurements showed that very high molar mass PIP could be obtained. For instance, with $AlEtCl_2$ or $AlEtCl_2/TiCl_4$ PIPs with molar masses up to 10^5 and 3.10^6 g/mol were measured, respectively [18,21]. Viscosimetric studies and LS measurements showed the formation of microgels through cross-linking reactions [24,28].

　　More recently, SEC was used to determine the molar masses of PIPs prepared in different polymerization conditions. At room temperature, molar mass distributions were generally broad (around 3–4) at low conversion and became broader and broader with increasing monomer conversion until becoming bimodal or even multimodal at high conversion (up to 40), M_n being always in the range 3000–16 000 g/mol [35,36,38,41]. With $TiCl_4/Cl_3CCOOH$ or $BF_3 \cdot Et_2O/Cl_3CCOOH$ as the initiating system, Rozentsvet and colleagues observed the formation of a high-molar-mass fraction (HMF) or a gel fraction (GF), coming from branching reactions at all the examined temperatures (20, –20, and –70 °C). It was shown that the HMF or GF started to form at lower conversion when decreasing the polymerization temperature (Table 8) [36,38]. Moreover, dispersity increased with polymerization time until gel formation, after which the molar mass and dispersity of the soluble fraction decreased. It was also shown that cross-linking reactions were dependent on the monomer and initiator concentrations, and on the [Ti]/[Cl_3CCOOH] ratio [35,36].

Table 8 Evolution of dispersity and GF fraction formation with conversion and polymerization time (adapted from [38]).

Conversion (%)	Polymerization temperature		
	20 °C	−20 °C	−70 °C
19.6	Monomodal	Monomodal	Polymodal
41.4	Monomodal	Polymodal	Gel
77.1	Polymodal	Gel	
98.2	Gel		

With 1-(4-methoxyphenyl)ethanol/B(C_6F_5)$_3$, Kostjuk et al. observed that, on the contrary, at −30 °C, molar masses increased (up to 5000 g/mol) with monomer conversion without noticeable changes in their molar mass distributions (around 3). It was assumed that by lowering the temperature a better controlled initiation took place followed by irreversible termination most likely due to proton elimination, with almost fully suppression of the competitive protic re-initiation which was important at room temperature. Thus, SEC analysis is commonly used to estimate the polymerization control over initiation, transfer, or branching reactions.

MALDI-TOF spectrometry
Very recently, matrix-assisted laser desorption/ionization with time-of-flight (MALDI-TOF) spectrometry was shown to be very useful to identify chain ends of cationic PIPs. It was thus demonstrated that PIP chains are mainly terminated by unsaturated DBs coming from transfer reactions [39,40]. With the cyclohexylidene alcohol/B(C_6F_5)$_3$ as initiating system for IP polymerization, Ouardad recently showed the contribution of both normal cyclohexylidene alcohol and protic initiation, characterized by the formation of PIP chains with cyclohexylidene and DMA chain ends, respectively [85]. In conditions where protic initiation was suppressed by adding a proton trap, they could also show that chain-to-chain coupling, which should yield to polymers bearing several cyclohexylidene groups, did not take place, suggesting that branching predominantly occurs in the presence of protons and results from attack of a proton on chain unsaturation. Chain-to-chain coupling yielding cross-linking and gel formation could then occur at higher monomer conversion and polymer concentration. Using 1-(4-methoxyphenyl)ethanol/B(C_6F_5)$_3$ as the initiating system, Kostjuk et al. [41] also showed that protic initiation was limited at low temperature and high at room temperature. In this case, chains bearing two initiator fragments were detected, but their formation was not attributed to chain branching but to a partial decomposition of the initiator after the ionization step of 1-(4-methoxyphenyl)ethanol to form *p*-methoxystyrene, which was then incorporated into the chain.

Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA)
Depending on polymerization conditions and on the extent of side reactions, the reported glass transition temperatures (T_g) of cationic PIPs vary significantly but are always higher than those of natural rubber (−72 °C) and gutta-percha (−63 °C) [86]. For instance, PIPs with T_g ranging from 57 to −34 °C are measured for polymerization performed at 20 °C down to −30 °C in CH_2Cl_2 using 1-(4-methoxyphenyl)ethanol/B(C_6F_5)$_3$ as the initiating system [41]. It is also mentioned in the literature the formation of triblock copolymers [poly(isoprene-*b*-isobutylene-*b*-isoprene)] via cationic sequential polymerization followed by full cyclization with TiCl$_4$ or BF$_3$·OEt$_2$, yielding PIP blocks with very high T_g (95–190 °C) [31].

Concerning their thermal stability, it is reported that cationic PIPs are stable to temperatures up to 350–380 °C and even to 410 °C when they are fully cyclized [14,15,31].

Thereby, with time, progress in cationic PIP characterization was achieved with the development of NMR, MALDI-TOF spectrometry but no appropriate analysis has been found yet to identify the precise structure of saturated sequences, which would allow the trail back to their mechanism of formation.

ACTIVE SPECIES, POLYMERIZATION MECHANISMS, AND CYCLE FORMATION

Both the exact nature of the active species and the mechanisms involved in the cyclic sequences formation have been discussed in many papers. Authors considered the contribution of different types of active species and mechanisms in order to tentatively explain the observed cationic reactions, their kinetics, and the structure of PIP. In the last part of this review, we will thus present the different interpretations proposed as well as the main works devoted to the elucidation of the structure of cyclic sequences.

Kössler et al. were the first to suggest that the active species involved in the IP cationic polymerization performed in the presence of $AlEtCl_2$ resulted from its ionized dimeric form $AlEt_2^+AlCl_4^-$, which was supported by conductivity measurements [14,17]. In order to explain the almost total disappearance of DBs during the polymerization, they suggested the formation of "cyclopolymers" through an ionic propagation mechanism as shown on Scheme 2, the few remaining DBs being located at chain ends [14]. In other studies, DB loss was attributed to the predominant formation of PIPs with 1,2- or 3,4-IP units that were readily cyclized [15]. The proposed structure of cationic PIPs was then that of a

Scheme 2 Various suggested cyclization mechanism during the IP cationic polymerization.

sequenced ladder-like/1,4-*trans*/ladder-like/etc. polymer with fewer than five fused rings in each "ladder block" [16].

Later, in the presence of $AlEtCl_2/TiCl_4$ as catalyst, it was proposed that $TiCl_2Et^+/AlCl_3\cdot AlCl_3Et^-$ or $TiCl_3Et\cdot AlCl_2^+/AlCl_3Et^-$ could be the active species that initiate IP polymerization. However, to better fit with experimental results, a mechanism involving cation-radical was suggested (Scheme 2) [20,21,24]. The propagation step involves 1,4 addition of the cation or the radical to the monomer followed by 3,2 addition of the cation or the radical to the residual DB. On Scheme 2, all other possible additions were intentionally omitted, although they could explain the very complicated ladder-like structures obtained. This cation-radical mechanism was partially supported by reduction of the polymerization rate in the presence of added benzoylperoxide or azobis(isobutyro)nitrile [21]. It was suggested, without any experimental proof, that the cyclic structures could correspond to perhydrophenanthrene sequences [21].

Some other type of active species were also proposed like the formation of charge-transfer complex when polymerizations were performed in nitrobenzene in the presence of $AlEtCl_2$ alone [22]. Besides, when $AlEtCl_2$ or $TiCl_4$ were used in the presence of protic compounds, protons were considered as the initiating active species [27,30]. Very recently, it was also shown, using dimethylallylbromide/$TiCl_4$ as initiating system, that the generated allylic carbocation could initiate IP polymerization [39].

Important efforts were made to characterize the structure of saturated/cyclic sequences and to know more about cyclization reaction mechanisms. As already mentioned, in the 1960s, the formation of saturated/cyclic sequences was first explained by the fact that the cationic IP polymerization could yield predominantly regioregular PIPs with 1,2- or 3,4-units that further underwent cyclization reactions. Later, it was admitted that 1,4-units, mostly *trans*, which are predominantly observed in uncyclized sequences, could also be subject to cyclization. This was supported by cyclization studies performed on various 1,4-*cis* and *trans* synthetic and natural rubbers. For example, Gordon determined the extent of cyclization of natural rubber in the presence of H_2SO_4 to be 86.5 % yielding di-isoprenic six-membered rings with one DB and 13.5 % of original 1,4-units remaining uncyclized [87]. It was proposed that cyclization proceeded by a mechanism involving adjacent IP units, while isolated 1,4-IP units were left as "widows" when they had no partners. This interpretation was supported by statistical calculations performed for similar reactions involving the contribution of adjacent units [88]. Moreover, it was also shown that a linear high-molar-mass PIP could be converted in relatively similar cyclization conditions into a much shorter polymer chain containing mono-, bi-, tri-, tetra-, and other polycyclic sequences distributed randomly throughout the backbone and separated by un-reacted IP units. The cyclization mechanism proposed for the formation of the different types of rings is shown in Scheme 3 [89]. Bi-, tri-, and tetra-substituted DBs are formed by elimination of a proton in β-position. Their relative proportion is decreasing in the order tetra- > tri- > di-substituted DBs [58]. Until now, only hypotheses have been made concerning the formation and structure of saturated rings. Some authors privileged the formation of monocyclic structures; others claimed the presence of polycyclic sequences [16,18,26].

In the 1990s, Priola and colleagues used mass spectrometry to identify the structure of cyclized sequences [32,33]. To this end, they studied the differences between cationic oligoisoprenes [polymerization degrees (DPs) up to 12] and their hydrogenated forms. Comparison of nonhydrogenated and hydrogenated oligomers permitted the determination of the average number of cycles (Gaussian curves centered on half of the DPs). It was shown that many isomers were formed. For example, for dimers, mainly α-pinene, p-cymene, and linear isomers were produced, the composition being dependent on the catalyst. For trimers, alkylhydronaphthalenes were produced with less linear structures. It was concluded that there was a random competition for the formation of cyclic and linear units, with, nevertheless, a higher probability to form cyclic units for low DPs.
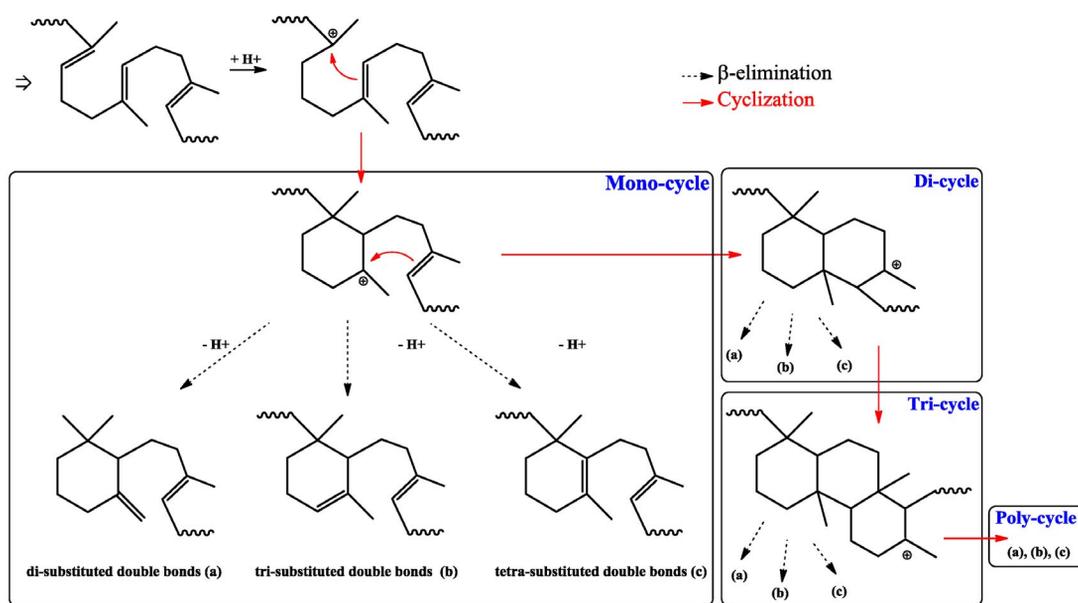
Scheme 3 Cyclization reaction mechanism involving 1,4-units.

As already mentioned, during cationic polymerization, the PIP molar masses generally increase with time. This was attributed to branching and gel formation through cross-linking reactions involving transfer reactions to the polymer. The polymerization solvent may also have a strong influence on these side reactions, since the formed PIP can be soluble or insoluble whether aromatic or aliphatic solvents are used. For example, with $AlEtCl_2/TiCl_4$, whereas in heptane no decrease of the polymerization rate was observed, in aromatic solvents, activity leveled off [24]. This was attributed to Friedel–Crafts reactions involving propagating species and the aromatic rings as it was shown that 2 phenyl rings were incorporated per 100 monomer units [21]. In chlorinated solvents, transfer reactions to the solvent can proceed as indicated by the presence of chlorine atoms on polymeric chains [25]. As a consequence of the transfer to solvent, cross-linking generally decreased.

Additives may also have a very strong effect. For example, the use of $AlCl_3$ in the presence of chlorinated additives yielded to a decrease of cross-linking and an increase of cyclic structures in aromatic solvents. They had no effect in dichloromethane, and both cross-linking and cyclization increased in hexane [34].

CONCLUSION

In this review, we reported and discussed literature data concerning the cationic polymerization of IP in the presence of various catalytic systems. The main common feature of PIPs obtained by this approach is their highly complicated and uncontrolled structures, which results from the presence of many side reactions (transfer, cyclization, cross-linking, and termination). Cationic PIPs can be seen as "copolymers" consisting of 1,4- and cyclized units, the structure of which is probably quite diverse. Up to now, attempts to control IP cationic polymerization (temperature, solvents, additives, etc.) have been unsuccessful and the characterization of the cationic PIP structures, in particular that of cyclized sequences, is still incomplete despite powerful analytic tools that are now available. A very recent improvement in this domain has, however, been achieved using quite unusual conditions for IP cationic polymerization, i.e., water dispersion [41]. In these conditions, PIPs exhibiting a very regular 1,4-*trans*

structure, with nevertheless still relatively low molar masses, have been obtained, suggesting that further progress in the control of IP cationic polymerization can reasonably be expected.

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