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Quasiliving Carbocationic Polymerization. XV. Forced Ideal Copolymerization of Isobutylene-Isoprene

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ABSTRACT

Forced ideal carbocationic copolymerization of isobutylene and isoprene has been achieved by continuous addition of monomer mixtures of different compositions to cumyl chloride/ TiCl_4 charges at -50°C . The overall rate of copolymerization could be kept equal to that of addition rate with up to 10 mol% isoprene in the mixed monomer feed. In this monomer concentration range the composition of the copolymer was identical to that of the feeds. At higher diene concentrations in the feed, chain transfer to mono-

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mer and other side reactions (intramolecular cyclization, gel formation) could not be completely avoided. The number-average molecular weight of the copolymers increased almost linearly with the amount of consumed monomers at 10 mol% isoprene concentrations in the feed (i.e., in the quasilinging range). According to $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy, the products are random copolymers.

INTRODUCTION

In conventional copolymerizations the composition of the charge and that of the copolymer product are different, except when both monomer reactivity ratios are equal to unity (a most rare circumstance) or with azeotropic charges. Under all other conditions the compositions will be different; moreover, during batch copolymerization the copolymer composition will continuously drift with decreasing monomer concentrations. Ideal copolymerizations are most desirable processes because under ideal conditions the composition of the charge and that of the copolymer are identical, and reactor control is immensely facilitated, particularly under continuous operations. The discovery that ideal copolymerizations can be achieved by slow continuous monomer introduction to an active charge so that the rate of monomer input and that of monomer consumption are equal, i.e., by the forced ideal quasilinging copolymerization technique [1], is of great value to the polymer scientist: He is now able by this technique to create many new random copolymers with relative ease.

The first phase of our investigations on forced ideal copolymerizations involved various styrene derivatives, i.e., monomer pairs whose reactivity ratios are very similar [1, 2]. Recently we extended our studies over monomers having quite dissimilar reactivity ratios. The isobutylene-isoprene pair appeared most interesting for this purpose not only because their monomer reactivity ratios are an order of magnitude apart, i.e., $r_{\text{IB}} = 2.5 \pm 0.5$, $r_{\text{IP}} = 0.4 \pm 0.1$ [3], but also because isobutylene-isoprene random copolymers (butyl rubbers) represent the most important commercial products prepared by cationic polymerization [4]. Butyl rubber is manufactured on a large scale by a continuous slurry process by feeding simultaneously into a stirred reactor a comonomer stream containing 3 vol% isoprene and the " H_2O "/ AlCl_3 initiating system, both dissolved in CH_2Cl_2 diluent at close to -100°C [4].

This paper concerns the forced ideal quasilinging copolymerization of various isobutylene-isoprene feeds at -50°C .

EXPERIMENTAL

Materials

Isobutylene (IB) was purified as described earlier [5]. Isoprene (Aldrich) (IP) was treated with NaOH solution to remove inhibitor, then washed with distilled water, dried over molecular sieves (3 Å), and distilled from CaH₂ under N₂. n-Hexane was refluxed with oleum to remove unsaturated impurities, then washed neutral with distilled water, dried over molecular sieves (3 Å), and distilled from CaH₂ under N₂. Methylene chloride was purified as described [6]. Cumyl chloride (2-chloro-2-phenyl propane) was prepared from purified α-methylstyrene by hydrochlorination in methylene chloride solution; excess HCl and solvent were removed by repeated freeze-drying. TiCl₄ was distilled from P₂O₅ under nitrogen.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N₂ at -50°C in 250 cm³ three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of the charge was 100 cm³ (60 cm³ n-hexane and 40 cm³ methylene chloride). Cumyl chloride initiator (10⁻³ mol) and TiCl₄ coinitiator (10⁻² mol) were added to the solvent mixture. The monomer mixture was introduced into the well-stirred charge by forcing it through a precision bore glass capillary by nitrogen pressure.

During the polymerization small aliquots (0.1 cm³) were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol. Conversions were determined gravimetrically.

Molecular weights were determined by a Waters Associates high pressure GPC equipped with five Microstyragel columns (10⁵, 10⁴, 10³, 5 × 10², and 10² Å) and dual UV/RI detectors. Molecular weights were calculated by the use of a calibration curve obtained with polyisobutylene standards.

Copolymer compositions were determined by integration of ¹H-NMR resonances using a Varian T-60 NMR Spectrometer and CDCl₃ solutions at room temperature. 20 MHz ¹³C-NMR spectra of two copolymers in CDCl₃ solution were recorded at room temperature using a

TABLE 1. FIQL Copolymerization of Isobutylene and Isoprene with Cumyl Chloride/TiCl₄ in n-Hexane/Methylene Chloride Mixtures (60/40 v/v at -50°C)

Sample	Cumulative amount of consumed monomers × 10 ³ mol	$\bar{M}_n \times 10^{-3}$	\overline{DP}_n	$P \times 10^3$ mol	MWD	Conversion (%)	IP content of copolymer (¹ H-NMR) (%)
Mole fraction of IP in feed: 0.02; $A_{IB} + A_{IP} = A - 4.1 \times 10^{-2}$ mol/min							
1/1	82	5.3	94	0.87	4.5		
1/2	164	9.2	164	1.0	4.2		
1/3	246	13.6	242	1.0	3.5		
1/4	328	17.4	310	1.05	3.7		
1/5	410	19.5	346	1.2	2.5	99	2.0
Mole fraction of IP in feed: 0.05; $A_{IB} + A_{IP} = A - 4.13 \times 10^{-2}$ mol/min							
2/1	83	3.7	65	1.3	1.6		
2/2	165	6.8	120	1.4	2.5		
2/3	248	8.7	153	1.6	3.4		
2/4	331	9.3	164	2.0	3.3		
2/5	414	10.6	188	2.2	3.1	99	5.1
Mole fraction of IP in feed: 0.10; $A_{IB} + A_{IP} = A - 4.03 \times 10^{-2}$ mol/min							
3/1	80.5	1.4	35	2.3	3.9		
3/2	158	2.4	42	3.8	4.6		
3/3	232	3.0	53	4.3	4.4		
3/4	306	3.7	65	4.7	4.3		
3/5	378	3.9	69	5.5	4.1	94	9.7

Mole fraction of IP in feed: 0.20; $A_{IB} + A_{IP} = A = 4.05 \times 10^{-2}$ mol/min

4/1	81	0.8	14	5.8	3.7
4/2	139	1.2	20	6.9	3.9
4/3	174	1.5	25	7.0	4.3
4/4	201	1.8	28	7.2	4.8
4/5	212	2.1	29	7.3	5.2
					18.3

Mole fraction of IP in feed: 0.50; $A_{IB} + A_{IP} = A = 4.02 \times 10^{-2}$ mol/min

5/1	45	0.7	11	4.1	3.9
5/2	79	0.8	14	5.6	4.1
5/3	101	0.95	15	6.8	4.4
5/4	120	1.2	18	6.6	4.9
5/5	135	1.2	19	7.1	5.8
					29
					46

Mole fraction of IP in feed: 0.80; $A_{IB} + A_{IP} = A = 4.05 \times 10^{-2}$ mol/min

6/1	42	0.41	6	7.0	2.9
6/2	69	0.49	8	8.6	3.6
6/3	97	0.58	9	10.8	3.7
6/4	104	0.62	9	11.6	4.2
6/5	127	0.68	10	12.7	6.6
					21
					67

Varian CFT-20 NMR Spectrometer. Typical acquisition parameters were: pulse width, 9 μ s; acquisition time, 0.511 s; pulse delay, 1.2 s, 1000K transients. Chemical shifts were measured relative to the central CDCl_3 line ($\delta = 77.0$ relative to tetramethylsilane).

RESULTS AND DISCUSSION

Led by previous experience in the field of quasiling polymerizations, we decided to start our investigations by feeding a stream of isobutylene-isoprene of various compositions into a charge of cumyl chloride/ TiCl_4 , both dissolved in 60/40 v/v $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ mixed solvents at -50°C . Table 1 shows the results and gives further experimental details. A series of six experiments have been carried out using the following isobutylene/isoprene feeds (in mole fractions): 98/2, 95/5, 90/10, 80/20, 50/50, and 20/80. The overall input rates (A) were similar (see $A_{\text{IB}} + A_{\text{IP}} = A$ values in Table 1) and aliquot samples were withdrawn regularly at 2-min intervals.

Monomer conversions were essentially 100% in the first three experiments, up to 10 mol% isoprene in the feed; however, monomer ac-

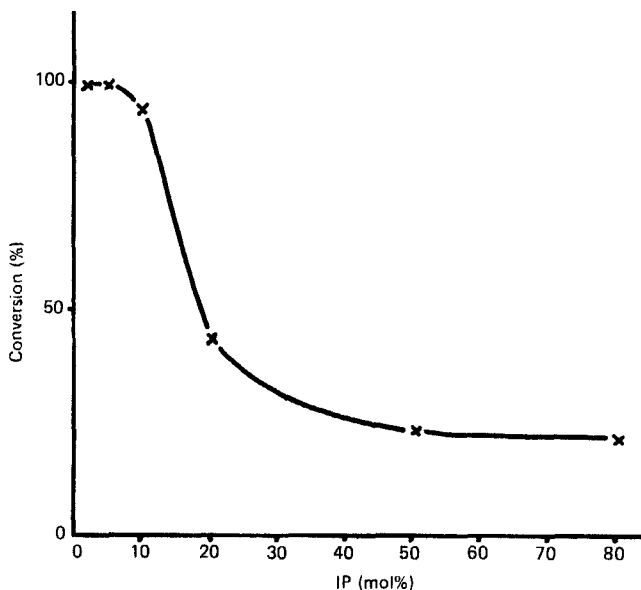


FIG. 1. Conversion vs IP mol% in feed plot in FIQL copolymerization of isobutylene and isoprene (according to data of Table 1).

cumulation occurred during the runs with higher isoprene concentrations (see 7th column in Table 1). Figure 1 is a plot of conversions versus isoprene concentration in the feed stream. The composition of the feeds and those of the copolymers (see 8th column in Table 1) were virtually identical over the entire concentration range although the conversions were quite different.

Figure 2 shows the \bar{M}_n versus comonomer input rate plot, and Fig. 3 the number of copolymer chains formed during the experiments.

Examination of these data indicates forced ideal copolymerizations in the experiments with 98/2, 95/5, and 90/10 isobutylene/isoprene feeds: complete monomer conversions (identity of feed and product

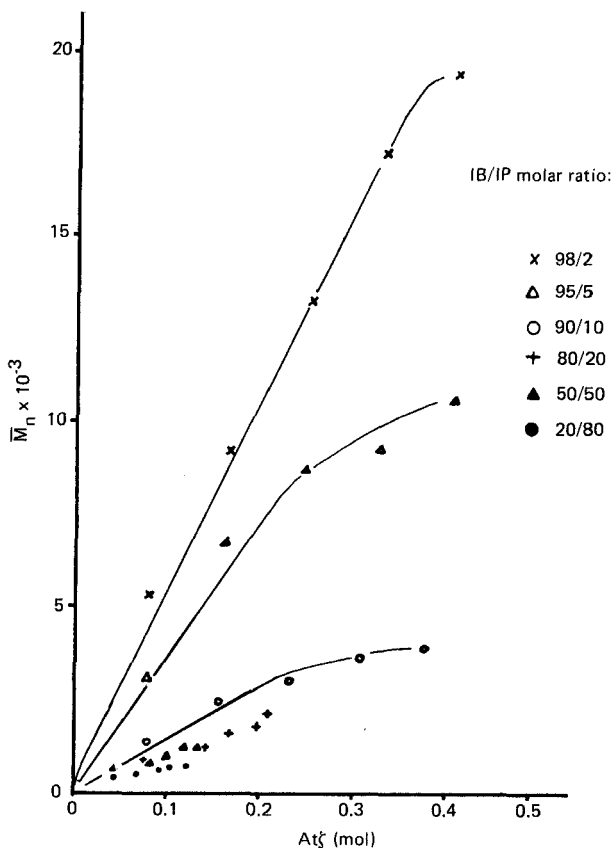


FIG. 2. \bar{M}_n vs cumulative amount of consumed monomer in the copolymerization of isobutylene and isoprene. ξ = conversion.

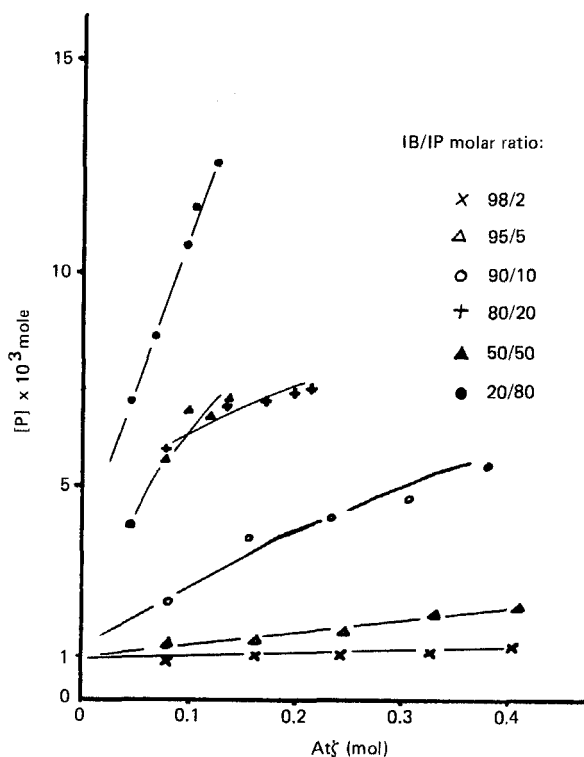


FIG. 3. Number of polymer molecules (P) vs cumulative amount of consumed monomer in the copolymerization of isobutylene and isoprene. ζ = conversion.

compositions) with concomitant linearly ascending \bar{M}_n versus monomer input plots passing through the origin.

The situation is not as clearcut with the feeds with higher isoprene concentrations: Although the feed and product compositions are identical, the monomer conversions are not 100% (unreacted monomer is accumulating in the charge). While the slopes of the linear \bar{M}_n versus monomer input plots show an ascending trend, it is difficult to assess whether they can be smoothly back-extrapolated to the origin (Fig. 2). The number of polymer chains formed during a run increases with increasing isoprene content in the feed quite strongly (Fig. 3). Evidently in the higher isoprene content range the basic forced ideal copolymerization kinetics still prevail (identity of feed and copolymer concentrations); however, effective chain termination starts to appear (lower

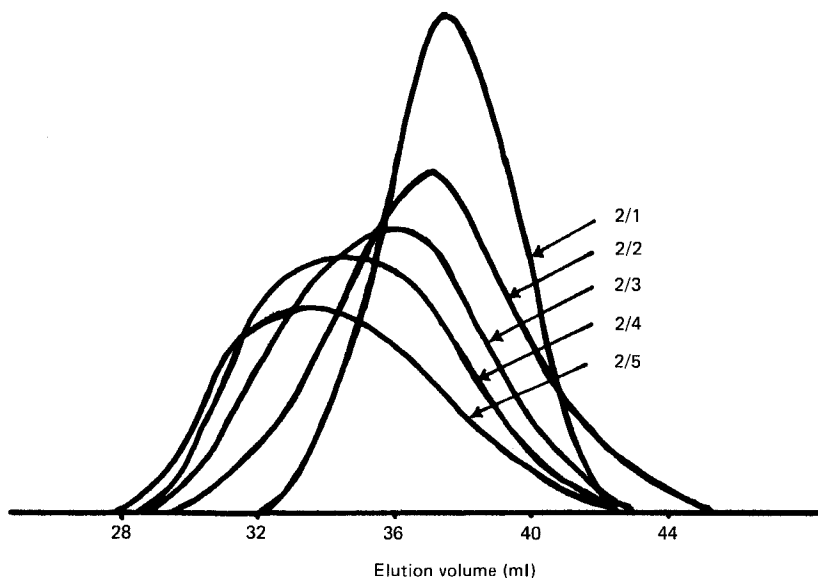
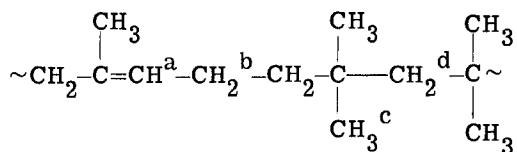


FIG. 4. GPC traces of samples 2/1, 2/2, 2/3, 2/4, and 2/5.

than 100% conversions) and chain transfer to monomer starts to operate (increasing $[P]$ during run).

The trends shown by the molecular weight distributions ($\overline{M}_w/\overline{M}_n$) are also revealing: While the $\overline{M}_w/\overline{M}_n$ values decrease in the first experiment (IB/IP = 98/2), they remain essentially unchanged and then increase, i.e., show an increasingly broadening trend with increasing isoprene concentrations in the feed (see 6th column in Table 1). Figure 4 shows the GPC traces of samples 2/1-5.

Inspection of the $^1\text{H-NMR}$ spectra of the final products shown in Figs. 5 and 6 indicate random copolymer formation. The resonances reveal the presence of peaks characteristic of random isobutylene-isoprene copolymer [7]. From the positions of resonances, the existence of the following structures can be written:



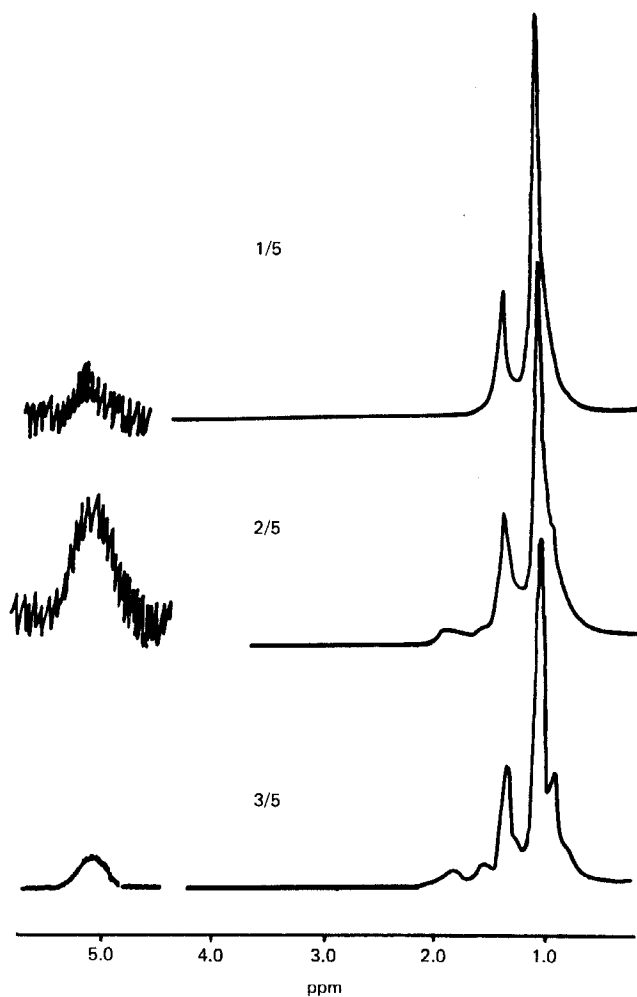
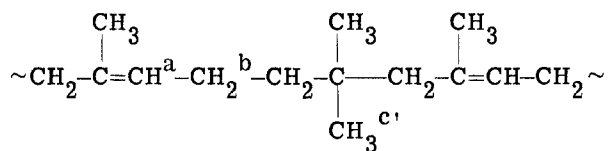


FIG. 5. ¹H-NMR spectra of various isobutylene-isoprene copolymers.

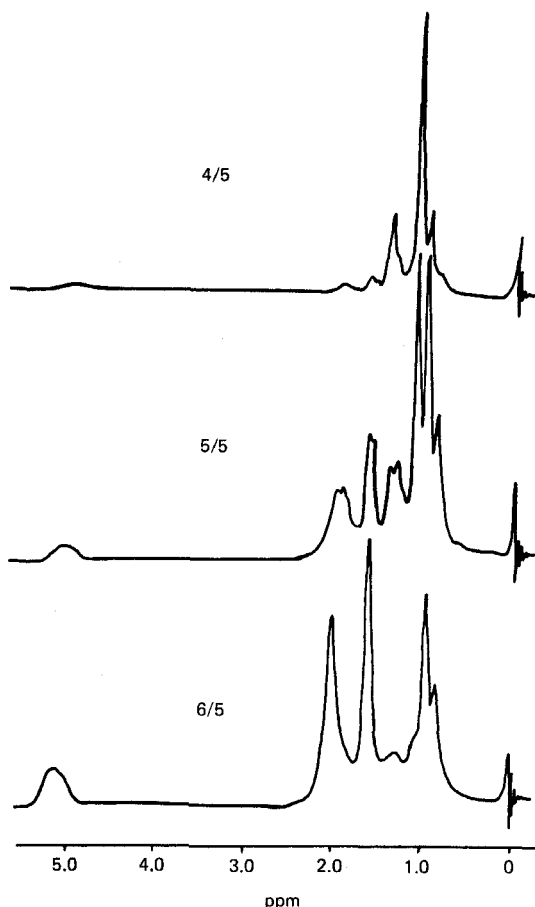


FIG. 6. ^1H -NMR spectra of various isobutylene-isoprene copolymers.

The chemical shifts of these characteristic protons are: 5.02 ppm (a); 1.31 ppm (b); 0.97 ppm (c); 0.86 ppm (c'); 1.40 ppm (d).

^{13}C -NMR spectroscopy also provides important information in regard to the structure of the copolymer. Figures 7 and 8 show spectra of two representative poly(isobutylene-co-isoprenes) containing 5 and 2 mol% isoprene, respectively. Table 2 is a compilation of structural elements, monomer sequences, and corresponding chemical shifts. The existence of mixed triads, tetrads, and pentads indicates that the copolymers are random in character.

These observations may be explained by considering the nature of

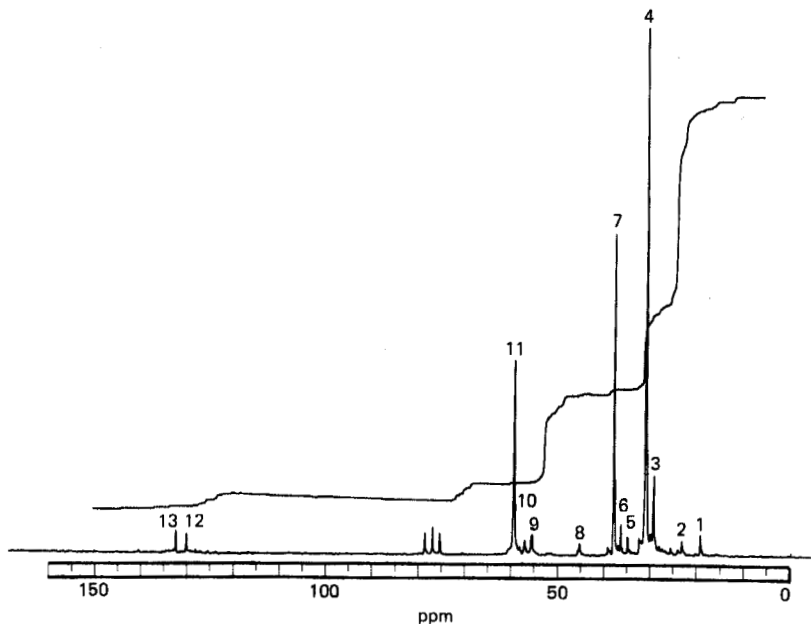
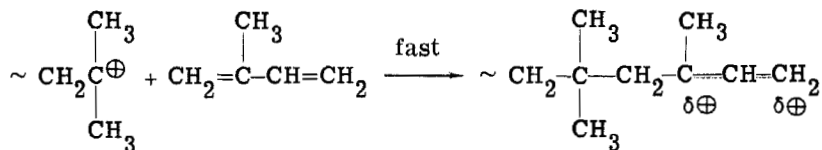


FIG. 7. ^{13}C -NMR spectrum of isobutylene-isoprene copolymer containing 5 mol% isoprene.

isobutylene-isoprene copolymerizations: The cumyl chloride/ TiCl_4 combination is a fairly efficient initiating system (the 2-chloro-2,4,4-trimethylpentane/ TiCl_4 system used previously with isobutylene-styrene is probably more efficient [2]). In the presence of relatively low amounts of isoprene, conversions are close to 100% and chain transfer is relatively unimportant; with increasingly larger quantities of isoprene, conversions decrease and chain transfer becomes important. Evidently cross-propagation from the isobutylene cation to isoprene must be rapid; however, that from the relatively stable isoprene cation to isobutylene is relatively slow [9, 10]:



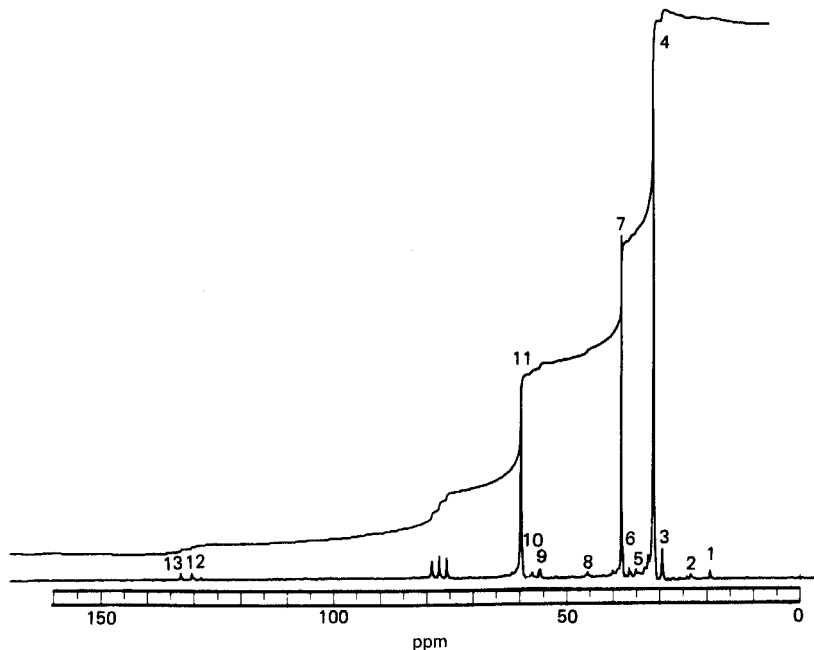
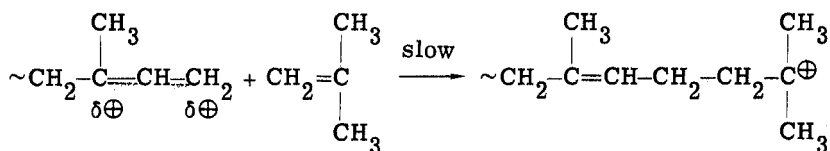


FIG. 8. ^{13}C -NMR spectrum of isobutylene-isoprene copolymer containing 2 mol% isoprene.



During the relatively slow $\text{IP}^{\oplus} + \text{IB}$ reaction, monomer may accumulate and (temporary) termination and/or proton expulsion may occur:

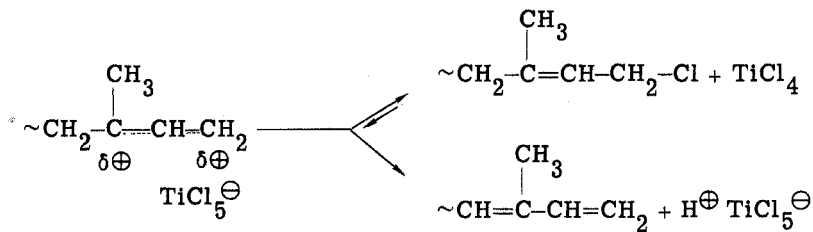


TABLE 2. ^{13}C -NMR Chemical Shifts (ppm) of the Isobutylene-Isoprene Copolymer^a

Peak	Carbon	Structure	Sequence	Chemical shift (ppm)
1	CH_3 (IP)		IB-IP-IB or IB-IP-IP	19.2
2	CH_2	$-\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}=\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-$	IB-IP-IB-IB or IP-IP-IB-IB	23.0
3	CH_3 (IB)		IB-IB-IP or IP-IB-IB	29.4
4	CH_3 (IB)		IB-IB-IB	31.5
5	C		IB-IP-IB-IB-IB or IP-IP-IB-IB-IB	35.0
6	C		IB-IB-IB-IP-IB or IB-IB-IB-IP-IP	36.6
7	C		IB-IB-IB-IB-IB	38.2
8	CH_2	$-\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}=\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-$	IB-IP-IB-IB or IP-IP-IB-IB	45.5
8	CH_2	$=\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-$	IP-IB-IB-IB	55.6
10	CH_2	$-\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}=\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-$	IB-IB-IB-IP	57.2
11	CH_2	$-\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-$	IB-IB-IB-IB	59.6
12	CH		IB-IB-IP-IB-IP, IB-IB-IP-IB-IB, IP-IB-IP-IB-IB, or IP-IB-IP-IB-IP	129.8
13	C		IB-IP-IP or IB-IP-IB	132.5

^aSee Ref. 8

In line with this analysis, the comonomer input rate should have been decreased with increasing isoprene content.

It is difficult to explain how the feed and copolymer compositions remain the same although monomer is accumulating in the reactor. Perhaps proton elimination is unimportant relative to termination (see above), or for some reason the expelled proton cannot reach the monomer supply (perhaps because the proton preferentially reacts with unsaturated in-chain isoprene copolymer units and the tight copolymer coils prevent monomer diffusion to the protonated units).

The fact that isoprene is a powerful chain transfer agent is also indicated by the results shown in Fig. 2: The rate of \bar{M}_n build-up decreases with increasing isoprene in the feed. Nonetheless, the \bar{M}_n growth obtained at low isoprene concentrations (< 10 mol%) is quite convincing and may be of interest for large-scale butyl copolymerizations, particularly if we consider that \bar{M}_n 's in excess of 17,000 ($\bar{M}_w > 43,000$) have rapidly been reached at -50°C . The experiment was discontinued at this stage because excessive viscosity increase rendered stirring difficult. The \bar{M}_n 's of isobutylene-isoprene (~ 2 mol%) copolymers obtained under conventional copolymerization conditions are much below these levels [9].

All the products were soluble, which is not too surprising in view of the low molecular weights obtained, particularly at high isoprene contents in the feed. The possibility of intramolecular cyclization exists.

Attempts of polymerizing pure isoprene feeds yielded gels. In the virtual absence of monomer (i.e., under quasiling conditions) the growing cations may attack in-chain unsaturations and would lead to cross-linked material, and the danger of cross-linking increases with increasing molecular weight. Further experimentation is needed to define suitable conditions for the synthesis of commercially acceptable high molecular weight random copolymers in the absence of disturbing gel formation.

ACKNOWLEDGMENTS

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