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CARBOCATIONIC POLYMERIZATION IN SUPERCRITICAL CO_2. IV.* THE ISOMERIZATION POLYMERIZATION OF 3-METHYL-1-BUTENE AND 4-METHYL-1-PENTENE

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ABSTRACT

The first carbocationic isomerization polymerization of 3-methyl-1-butene and 4-methyl-1-pentene in supercritical carbon dioxide ($SC{\cdot}CO_2$) has been demonstrated. The use of the "H_2O"/$AlCl_3$ initiating system at 32.5°C readily gives ~40% conversions of poly(3-methyl-1-butene) of M_n = 1000 (M_w/M_n = 1.41), and ~70% conversions of poly(4-methyl-1-pentene) of M_n = 1700 (M_w/M_n = 2.16). According to IR spectroscopy the degrees of isomerization in $SC{\cdot}CO_2$ at 32.5°C are similar to those occurring in conventional liquid systems at much lower temperatures. The nature and mechanism of side reactions are discussed.

INTRODUCTION

The first synthesis of a crystalline poly(3-methyl-1-butene) by cationic isomerization polymerization was reported by Kennedy and

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[*] For Part III of this series of publications see Deak et al., Polym. Bull., 33, 259, (1994)

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Thomas [1]. In subsequent papers it was shown that the cationic polymerization of 3-methyl-1-butene produces a "copolymer" of 1,2 (-CH_2-$CHCH(CH_3)_2$-) and 1,3 (-CH_2-CH_2-$C(CH_3)_2$-) units and the polymerization of 4-methyl-1-pentene gives rise to a complex structure of 1,2 (-CH_2-$CHCH_2CH(CH_3)_2$-), 1,3 (-CH_2-CH_2-$CHCH(CH_3)_2$-) and 1,4 (-$(CH_2)_3$-$C(CH_3)_2$-) units [2-6]. The relative ratio of these repeat units is determined by the relative rates of isomerization and propagation. The relative amounts of 1,3- and 1,4- i.e., the completely isomerized repeat units in the polymerization of 3-methyl-1-butene and 4-methyl-1-pentene, respectively, decrease with increasing temperature because the activation energy of propagation by the secondary carbocations is lower than that of isomerization by hydride shift [6].

There is a dearth of information relative to Friedel-Crafts isomerization in supercritical fluids. Kramer [6] demonstrated isomerization of paraffins in supercritical carbon dioxide (SC•CO_2) and found that for example the isomerization/cracking ratio in the $AlBr_3$ catalyzed isomerization of n-hexane in SC•CO_2 was 5:1 whereas in the homogeneous liquid phase this ratio was 1:1. Evidently, the selectivity toward the formation of isomerized products increases under supercritical conditions.

Against this background and in the framework of our fundamental investigations on cationic polymerization in SC•CO_2, we became interested in exploring the isomerization polymerization of 3-methyl-1-butene and 4-methyl-1-pentene. This paper concerns an exploration of the polymerization behavior of these branched olefins in SC•CO_2 at 32.5°C.

EXPERIMENTAL

The source of chemicals used, the apparatus and the experimental technique have been described in detail [8,9]. 3-Methyl-1-butene and 4-methyl-1-pentene were received from Aldrich and Lancaster, respectively, and used without further purification. Briefly, the polymerizations were carried out in a high pressure, Hastelloy C (Parr) reactor. The reactor was charged under dry nitrogen in a dry box with the needed amount of monomer (3-methyl-1-butene or 4-methyl-1-pentene), cosolvent (methyl chloride (MeCl) or ethyl chloride (EtCl)) and with a sealed ampoule containing a mixture of 2-chloro-2,4,4-trimethylpentane (TMPCl)/Friedel-Crafts acid ($TiCl_4$, BCl_3) initiating system. The ampoules were prepared prior to experimentation in a dry box under a blanket of dry nitrogen. The $AlCl_3$ coinitiatior solutions were also prepared in the dry box by placing ~1.0 g $AlCl_3$ in 30 mL EtCl at -30°C, stirring the mixture for 1 hr at this temperature, filtering, transferring the predetermined portions of the saturated solutions into ampoules, and sealing under nitrogen. The concentration of the saturated EtCl solutions was 1.2% $AlCl_3$. After assembling the polymerization system [8] the reactor was heated to 32.5°C and pressurized with CO_2 to 140 bar. The polymerization of 3-methyl-1-butene was homogeneous in every experiment. In contrast, the polymerization of 4-methyl-1-pentene under the same conditions was heterogeneous i.e., hydrocarbon (monomer/polymer) droplets were observed to float in the stirred SC-CO_2 continuous phase. A substantial decrease of pressure (~20 bar) was noted during the polymerizations. The visual observations were made by means of a video camcorder [8].

The analytical methods (GPC, NMR) used in this work have been described [8,9]. IR spectra were taken on a Nicolet 55 XC FT-IR spectrometer. All spectra were taken on polymer films on a NaCl window.

RESULTS AND DISCUSSION

1. Polymerization results

Table 1 summarizes conditions and results of 3-methyl-1-butene and 4-methyl-1-pentene polymerization. Expts 1 and 2 (Table 1) show the results of attempted polymerization of 3-methyl-1-butene by the TMPCl/($TiCl_4$/BCl_3) and TMPCl/$TiCl_4$ initiating systems, respectively. The essential absence of poly-merizations under these conditions is most likely due to the low rate of cationation by the TMP^+. Higher molecular weights were obtained with the "H_2O"/ $AlCl_3$ system (Expts 3-5). Conversions increased by increasing the

TABLE 1

Polymerization conditions and results of isomerization of 3-methyl-1-butene and 4-methyl-1-pentene in supercritical carbon dioxide (P=140 bar, T=32.5°C)

Exp	Monomer mole	Cosolvent vol%	Initiator* mole	$TiCl_4$ mole x 10^2	BCl_3 mole x10^2	$AlCl_3$ mole x10^3	Time hrs	Conv %	M_n** g/mole	M_w/M_n
				3-methyl-1-butene						
1.	0.232	MeCl 5	TMPCl 0.003	2.73	5.1	-	3	0	-	-
2.	0.241	MeCl 10	TMPCl 0.003	2.73	-	-	24	2	oligomers	-
3.	0.268	EtCl 6	"H_2O"	-	-	0.9	24	3	~1000	1.88
4.	0.268	EtCl 10	"H_2O"	-	-	2.9	24	25	~1000	1.47
5.	02.68	EtCl 10	"H_2O"	-	5.1	2.9	64	41	~1000	1.41
				4-methyl-1-pentene						
6.	0.196	EtCl 10	"H_2O"	-	5.1	2.9	3	60	~1700	2.20
7.	0.196	EtCl 10	"H_2O"	-	5.1	2.9	24	70	~1700	2.16

*In experiments 1 and 2 the initiator was 2-chloro-2,4,4-trimethylpentane (TMPCl), in experiments 3-7 the polymerization started by means of advenititious water ("H_2O").

** By GPC, with polyisobutylene as calibrant

$AlCl_3$ concentration and ~41% conversion was achieved after 64 hrs polymerization (Expt 5). Polymerization time and monomer conversion do not seem to affect molecular weights (Expts 4 and 5) which suggests that the molecular weight determining event during the polymerization is chain transfer to monomer even in the presence of the $AlCl_3/BCl_3$ mixed system (Exp 5). This result is in contrast with our earlier results [9] obtained with isobutylene polymerization coinitiated by mixtures of $TiCl_4/BCl_3$ for the synthesis of $-Cl^t$ ended polyisobutylenes. The terminal $-Cl^t$ in the experiments with isobutylene was due to fast Cl^- exchange between

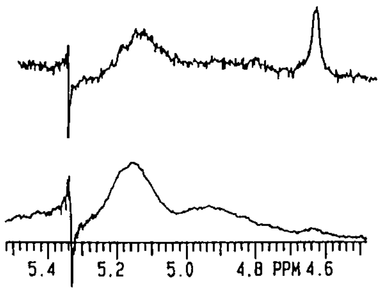
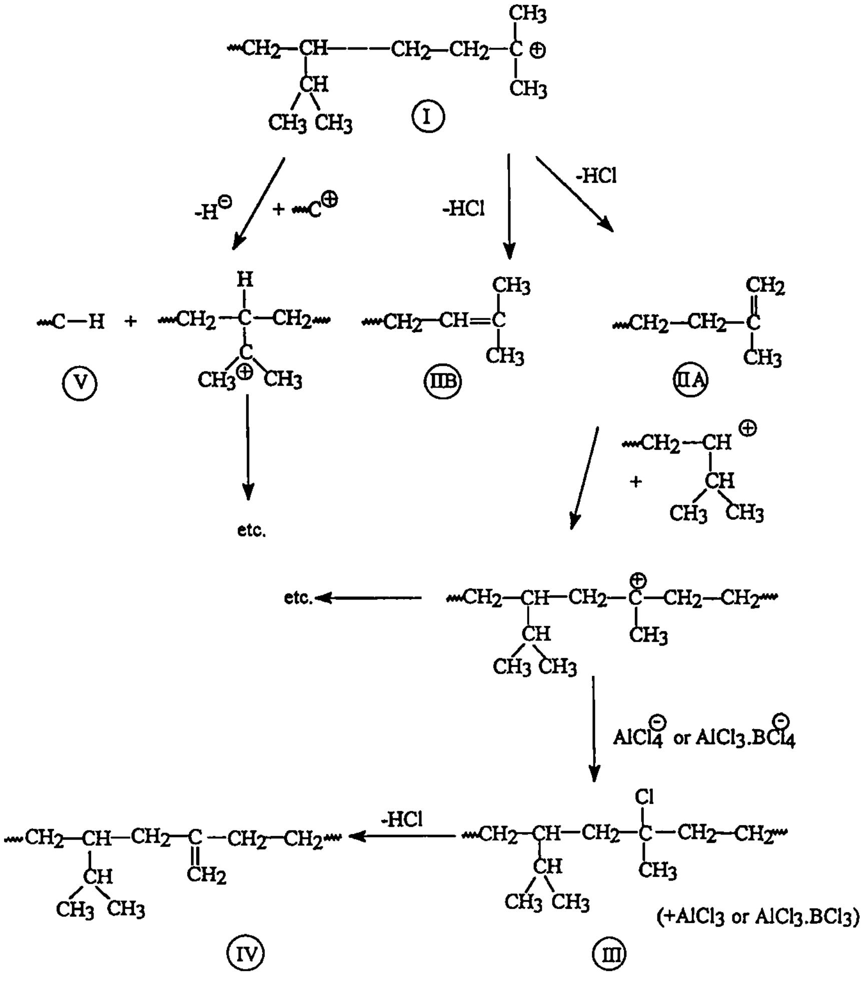


Figure 1. Olefinic region of ^1H NMR spectra of poly(3-methyl-1-butene) obtained in SC•CO_2 (Expt 5 in Table 1, see text for assignments)

$TiCl_5^-$ and BCl_3 followed by termination by chlorination. This type of Cl^- exchange probably does not occur in the $AlCl_3/BCl_3$ system because the stability of the $AlCl_4^-$counteranion is superior to that of $TiCl_5^-$.

The same conclusions can be reached in respect to 4-methyl-1-pentene polymerization by considering the results of Exps 6 and 7: Although the conversion increased with increasing time, the polymer molecular weights did not change indicating extensive chain transfer to monomer.

According to ^1H NMR spectroscopy, the poly(3-methyl-1-butene) obtained in Expt 5 contains significant amounts of unsaturation (see Figure 1) which is evidence for proton elimination during polymerization. The singlet at 5.15 ppm is characteristic of $-CH_2-C\underline{H}=C(CH_3)_2$ protons. After dehydroclorination the sample showed a small well-defined singlet at 4.65 ppm indicating the presence of non-terminal $=CH_2$ groups (Figure 1) which arose upon HCl loss of various non-terminal -Cl^t groups. The spectrum does not show evidence for terminal-Cl^t's (absence of resonances at 4.6 and the 4.8 ppm) but shows the presence of low concentration of in-chain Cl^t's. Scheme 1 outlines the reactions envisioned to account



SCHEME 1
Polymerization of 3-Methyl-1-Butene: Possible Reactions that Explain Available Structural Information

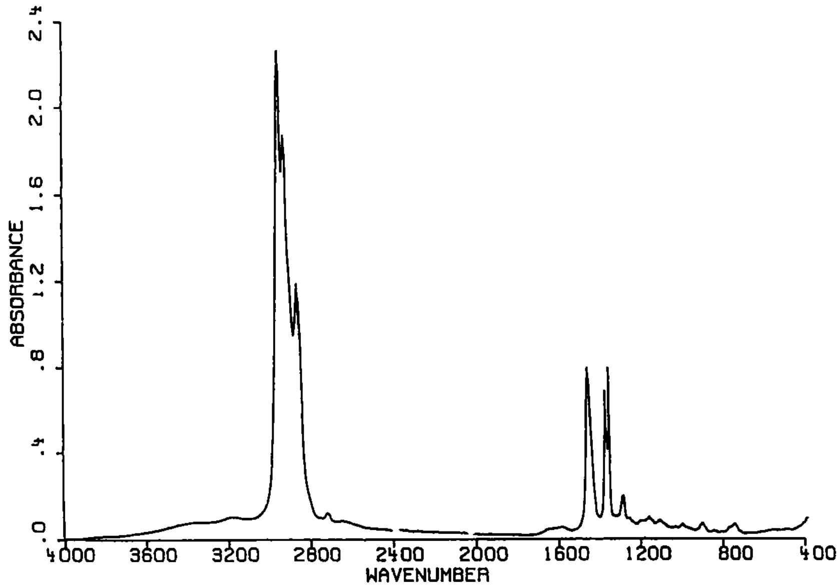


Figure 2. The IR spectrum of poly(3-methyl-1-butene) synthesized in Expt 5, Table 1; Assignments in Table 2

for the structural findings. At the relatively high temperature of these polymerizations the growing polymer chain (I) may rapidly loose H^+ and gives terminal olefin IIA and IIB. The exo-olefin competes for growing carbocations during the polymerization and forms a sterically hindered carbocation (see arrow) which undergoes termination by chlorination to give III. The latter (III) is a precursor of the internal olefin detected by ^1H NMR after dehydrochlorination. Scheme 1 also outlines a possible hydride abstraction leading to chain termination [8].

2. Infrared spectroscopy

Figure 2 shows the IR spectrum of a representative poly(3-methyl-1-butene) obtained in SC•CO_2 and the major assignments are listed in Table 2 [3]. The IR spectra of poly(3-methyl-1-butene) and poly(4-

TABLE 2

IR assignments of Poly(3-methyl-1-butene) [3]

1/λ (cm^{-1})	Intensity*	Assignment
2960	vs	CH hydrogen streching, -CH, - CH_2 , -CH_3
2931	vs	
2867	w	
2730-31	w	
1647	s	
1469	s	CH_2 hydrogen bending modes
1387	s	CH_3 sym. hydrogen bending modes
1364	s	CH_3 sym. hydrogen bending modes
1283	m	-CH_2-CH_2- twisting (or wagging vibrations)
1199	sh	internal quaternary carbon atom
1162	w	internal quaternary carbon atom or/and isopropyl
1099	w	internal quaternary carbon
1012	w	
894	w	
745	w	-CH_2-CH_2- skeletal rocking mode

* s-strong, m-medium, w-weak, sh-shoulder

methyl-1-pentene) prepared under the same conditions in SC•CO_2 are essentially identical. All the polymers showed characteristic C-H stretching vibrations between 3000 and 2700 cm^{-1}. The region between 2700 and 1500 cm^{-1} is relatively transparent. A weak unidentified peak appears in all samples at 2730 cm^{-1}. The $-CH_2-$ and $-CH_3$ hydrogen bending vibration gave a strong absorption at 1469 cm^{-1}. The most important part of the IR spectra of these polymers is the region between 1400 and 1200 cm^{-1} . The intensity of the absorption at 1382 cm^{-1} is lower than that at 1364 cm^{-1} which is [3,10] characteristic of *gem*-methyl groups. In isotactic poly(3-methyl-1-butene) and hydrogenated 3,4-polyisoprene these bands are of equal intensity indicating the presence of isopropyl groups [3]. The difference between the intensities of absorptions at 1382 and 1364 cm^{-1} suggests that the polymer contains substantial amounts of completely isomerized 1,3-(in poly(3-methyl-1-butene)) and 1,4-repeat units (in poly(4-methyl-1-pentene)), together with the conventional 1,2-unit in poly(3-methyl-1-butene), and 1,2- and 1,3-units in poly(4-methyl-1-pentene). This conclusion is further supported by the presence of the 1283 cm^{-1} adsorption characteristic of the $-CH_2-CH_2-$ group [3,10], present only in isomerized units in poly(3-methyl-1-butene) and poly(4-methyl-1-pentene). Further strong evidence for isomerization is also the small but characteristic absorption at 745 cm^{-1} due to the $-CH_2-CH_2-$ groups [3]. Quantitative conclusions in regard to the microstructure of cationically prepared poly(3-methyl-1-butene) and poly(4-methyl-1-pentene) could not be made because of the absence of appropriate calibration.

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