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An Investigation of the Structure of Copolymers of Isobutylene and Diene Prepared by Initiation with VCl_4 in the Dark and with Visible Light

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ABSTRACT

^{1}H-NMR spectra of copolymers of isobutylene and 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene were investigated in connection with the elucidation of the formation of soluble and insoluble copolymers. For copolymers soluble in heptane, benzene, and CCl_4 it was found that the incorporation of diene into the polymer chain proceeds by 1,4-addition in the case of copolymerizations conducted both in the dark and with visible light using VCl_4 as initiator. The formation of a soluble and an insoluble copolymer is attributed to a different type of initiation, either with radical-cations of isobutylene, if soluble copolymers are formed, or with radical-cations of diene, if the arising copolymers are insoluble.

INTRODUCTION

In another paper [1] we described the polymerization of isobutylene (IB) initiated with VCl_4, which in nonpolar solution without a protonic co-initiator in the dark and at temperatures lower than -20°C proceeds only after the addition of such dienes as 1,3-butadiene

(B), isoprene (IP), and 2,3-dimethylbutadiene 1,3 (DMB). After the addition of butadiene or isoprene, insoluble copolymers are formed, while the addition of DMB leads to the formation of soluble copolymers [1]. In the same paper [1] we reported that only soluble copolymers are formed under the same conditions by the light-initiated copolymerization of isobutylene with isoprene or butadiene. Soluble copolymers (in heptane, benzene, CCl_4) are also formed in the copolymerization in methyl chloride (monomer concentration $\leq$ 65 wt%), both in the dark and with light. On the other hand, at temperatures above -9° C only soluble copolymers are formed in nonpolar medium, even in the dark.

In order to find out to what extent the polarity of the medium or the effect of light may affect the structure of butyl rubbers, we used ^{1}H-NMR spectroscopy to examine the structure of a soluble sample of the isobutylene-isoprene copolymer prepared in the dark in bulk (at -9° C) and in methyl chloride solution (at -25° C). For samples of the copolymer of isobutylene and isoprene, prepared in heptane solution by copolymerization with visible light at temperatures below -20° C, it was established earlier [2] that isoprene enters the polymer chain by 1,4-addition.

The structures of copolymers of isobutylene with butadiene and of isobutylene with DMB were studied for copolymer samples prepared by initiation with VCl_4 in bulk at -40° C in the dark and with light.

EXPERIMENTAL

Samples of copolymers were prepared by polymerization initiated with VCl_4 by employing a procedure described in another paper [1]. Characteristic parameters of samples used in measurements of the ^{1}H-NMR spectra are given in Table 1. Even after dissolution in CCl_4 lasting several days (10 d at 65° C), Sample IB-IP-1 contained a small quantity of gel particles which were removed by filtration before the measurement, because gel particles impaired the resolution of the ^{1}H-NMR spectrum. Sample IB-B-1, the dissolution of which in CCl_4 also took several days, contained fine gel particles in a major amount which were not removable by filtration. On the contrary, Samples IB-IP-2, IB-B-2, IB-DMB-1, and IB-DMB-2 were completely soluble in CCl_4.

Measuring Technique

High-resolution ^{1}H-NMR spectra were recorded with a JEOL PS-100 spectrometer at 100 MHz and 65° C. The measuring cells were filled with 30% (w/v) solutions of copolymers of isobutylene with dienes in CCl_4. The solutions were prepared by stirring in sealed cells at 65° C for 12 h.

TABLE 1. Characteristic Parameters of Samples of Poly(isobutylene-co-isoprene), Poly(isobutylene-co-1,3-butadiene), and Poly(isobutylene-co-2,3-dimethyl-1,3-butadiene)[a]

Wt % of comonomer in monomeric mixture	T (°C)	Polymerization	C (%)	$\overline{M}_\eta \times 10^{-3}$	u (mol%)	Sample
1.0 IP (dark)	-9	Bulk	52	34.5	0.9	IB-IP-1
3.0 IP (dark)	-25	CH_3Cl[b]	86	71.0	1.3	IB-IP-2
10.0 B (dark)	-40	Bulk	46	ins		IB-B-1
15.0 B (light)	-40	Bulk	36	490.0	1.3	IB-B-2
3.0 DMB (dark)	-40	Bulk	28	220.0	2.1	IB-DMB-1
3.0 DMB (light)	-40	Bulk	33	220.0	2.2	IB-DMB-2

[a] IP = isoprene, B = butadiene, DMB = 2,3-dimethyl-1,3-butadiene, T = polymerization temperature, C = conversion, u = unsaturation, ins = insoluble polymer, dark = polymerization in the dark, light = polymerization with visible light, $\overline{M}_\eta$ viscometric molecular mass of the polymer.

[b] Monomer concentration in methyl chloride solution was 40 wt%.

The unsaturation of copolymer samples was determined ozonometrically [1]. The viscometric determination of molecular mass ($\overline{M}_\eta$) has also been described in another paper [1], along with the purification and drying of monomers, solvents, argon, and VCl_4.

RESULTS

The Structure of Copolymers of Isobutylene with Isoprene

The ^{1}H-NMR spectra of Samples IB-IP-1 and IB-IP-2 are given in Fig. 1, where they are compared with the measured spectrum of the butyl rubber sample Polysar Butyl 301.

Intensive bands in the spectrum recorded at a low amplification (Fig. 1a) situated at 8.89 τ and 8.58 τ correspond to the resonance of the methyl and methylene protons of isobutylene units. In spectra recorded at high amplification, a band at 5.0 τ also can be distinguished, as shown in Fig. 1 (Spectrum b, c, d). The position and shape of the band (a singlet) at 5.0 τ are the same for all samples under investigation and indicate that this band is due to the vinylene proton of 1,4-isoprene units [2-4]. The positions of bands at the bottom of the

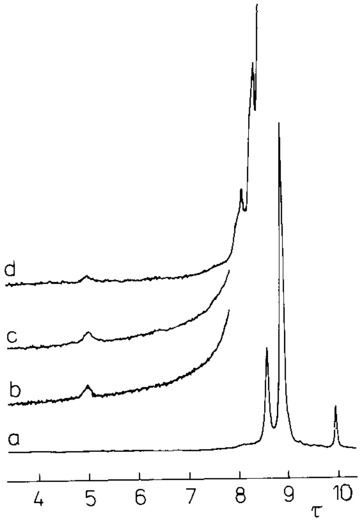

FIG. 1. ^{1}H-NMR spectra of copolymers of isobutylene with isoprene: Polysar butyl 301 (a, b), IB-IP-2 (c), and IB-IP-1 (d). Measured in CCl_4 solution at 30% (w/v) concentration at 65°C at low (a) and high (b, c, d) amplification.

intensive band of isobutylene protons at 8.38τ and 8.09τ (Fig. 1d) also correspond to the methyl and methylene protons of 1,4-isoprene units [2, 3].

The integrated band intensities at 5.0τ of spectra recorded under identical conditions (Fig. 1b, c, d) are in agreement with the unsaturation values determined independently for the samples under investigation.

The Structure of Isobutylene-Butadiene Copolymers

The ^{1}H-NMR spectrum of Sample IB-B-1 exhibits a single, very broad band, without any fine structure. The width of this band, $\Delta\nu$, measured at half the maximum height ($\Delta\nu \approx 200$ Hz), is larger by an order of magnitude than the bandwidth of isobutylene protons of Sample IB-B-2. Such NMR behavior is frequently met within samples which contain swollen gels of cross-linked polymers, and the chemical structure could not therefore be investigated.

The ^{1}H-NMR spectrum of Sample IB-B-2 at high amplification exhibits a band at 4.7τ and another band at 7.7τ, situated at the bottom of the intensive band of isobutylene protons. In the range ~5τ, the single observed band at 4.7τ corresponds to the CH protons of butadiene units in the 1,4-structure. The spectrum does not show any bands at ~5 τ which would suggest the presence of 1,2-structures. 1,4-Structures are also confirmed by the band of CH_2 protons of butadiene units at 7.7 τ.

The Structure of Copolymers of Isobutylene and 2,3-Dimethylbutadiene-1,3

The ^{1}H-NMR spectra of Samples IB-DMB-1 and IB-DMB-2 are virtually identical. Although the unsaturation of the samples (2.1, 2.2, mol%) is higher than that of the samples of the Copolymers IB-IP and IB-B, the 1,2-structure was not detected in the spectra (structure 1,2 containing vinyl protons would be reflected in a band at ~5 τ), and everything indicates that only the 1,4-structures are reflected in the spectra.

DISCUSSION

For all samples of copolymers of isobutylene with IP, B, and DMB soluble in heptane, benzene, and CCl_4 it was found that the diene units enter the polymer chain by 1,4-addition. At the same time, the 1,4-structure was detected for samples prepared in the dark and with light [poly(isobutylene-co-isoprene) and poly(isobutylene-co-2,3-dimethyl-1,3-butadiene)], as well as for samples prepared in polar and nonpolar medium [poly(isobutylene-co-isoprene)].

The different mechanism of initiation in the copolymerization of isobutylene with IP or B in nonpolar medium initiated with VCl_4 is one of the alternatives allowing us to explain the formation of a soluble copolymer (copolymerization with light) in one case and of a cross-linked copolymer (copolymerization in the dark) at temperatures below -20°C. In the formation of soluble copolymers (formed also by the copolymerization of isobutylene with IP or B in the dark in methyl chloride solution), the initiation is probably started by radical-cations of isobutylene, while in the formation of insoluble copolymers the initiation is probably started by radical-cations of the diene comonomer. In all these cases the copolymerizations are inhibited by oxygen [1]. This view is based on the finding that in a mixture of isobutylene with IP ([isobutylene] = 8.64 mol/L, [isoprene] = 0.36 mol/L, [VCl_4] = 3×10^{-2} mol/L), the irradiation with visible light in the presence of VCl_4 gives rise to a signal in the ESR spectrum, which corresponds to radical-cations of isobutylene [2]. For this reason, copolymerization with light is initiated by radical-cations of isobutylene. On the contrary, in the dark, when the polymerizations of isobutylene alone in the presence of VCl_4 at temperatures below -20°C do not proceed and are started only after the addition of diene, initiations obviously proceed through radical-cations of the respective dienes [1].

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