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SYNTHESIS AND 500 MHz-NMR CHARACTERIZATION OF POLY(2-TRIMETHYLSILOXY)BUTADIENE OBTAINED BY FREE RADICAL AND CATIONIC POLYMERIZATIONS

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Abstract—2-(Trimethylsiloxy)butadiene was polymerized in the presence of AIBN, using different conditions of dilution and temperature. The resulting polymer was characterized by ^{1}H- and ^{13}C-NMR: in particular, DEPT and ^{1}H–^{13}C correlation spectra allowed to assign the different microstructures with high confidence. *Cis*- and *trans*-1,4-microstructures and 3,4-microstructure were observed in all cases, but 1,2-microstructure was never detected. The evolution of microstructure ratios with temperature was found to differ from the evolution described for other 2-substituted butadienes. Molecular weights determined by GPC are low to moderate in all cases ($M_n < 10^4$) decreasing with increasing temperature. Attempts to polymerize the monomer in the presence of cationic initiators failed to give a polymer, except when $SnCl_4$ was used.

INTRODUCTION

A classical access to reactive-polymers is the polymerization of functionalized monomers bearing reactive groups [1, 2]. When the considered functionalized monomer is a 1,3-butadiene substituted on position 2 by a polar group and when the resulting microstructure is 1,4 or 3,4, a polybutadiene that incorporates the polar group on the residual C=C double bond can be obtained (Fig. 1). At such a position, the polar group can activate the double bond to enable further chemical modification of the polymer, including grafting and cross-linking.

From that point of view, trialkylsiloxy substituents ($X = R_3SiO$) are particularly attractive as polar groups because the nucleophilic reactivity of silylated enol ethers toward a great variety of electrophiles has been extensively described in the literature and has proven to be a valuable synthetic moiety [3, 4]. Furthermore 2-(trialkylsiloxy)butadiene are extremely easy to synthesize in one step from the readily available methyl vinyl ketone and trialkylsilyl chlorides.

A preliminary report on the polymerization of 2-(trimethylsiloxy)butadiene (TMSBD), was reported in the literature a few years ago [5]. Unfortunately, only one experimental condition for the homopolymerization (bulk, 5 mol% AIBN, 60°, 120 hr) was investigated. The resulting polymer was attributed a weight average molecular weight of 1.12×10^4 as determined by GPC, but neither the number average molecular weight nor the polydispercity were given. The polymer had 18.6% of 3,4-structure, 0.0% of 1,2-structure, and 81.4% of 1,4-structures (*cis*/*trans* ratio not described). These last results were based on the ^{1}H-NMR of the polymer in $CDCl_3$, assuming that the relative position of chemical shifts for vinylic protons is just as for poly(isoprene) vinylic protons.

Possible use of poly(TMSBD) as a reactive-polymer is largely dependent on the accessible range of molecular weights and polydispersities, on the presence of structural defects, and on the microstructure. All these characteristics are known for other 1,3-butadienes to be highly dependent on the conditions used during the polymerization. We thus decided to completely reinvestigate the radical homopolymerization of TMSBD under different conditions and to determine how much these conditions affect the structure and molecular weight characteristics of the resulting polymer.

EXPERIMENTAL PROCEDURES

(A) Materials

2-Trimethylsiloxybutadiene (TMSBD) was synthesized from methyl vinyl ketone according to a published procedure [6]. GC analysis of the monomer showed traces of hexamethyldisiloxane and trimethylsilanol; the area of these two impurities however involves <1% of the total area. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All cationic initiators are commercial and were used as received. The toluene used for the cationic polymerization was distilled over sodium.

(B) Polymerization

Radical polymerization. All polymerization were carried out in sealed glass ampoules under argon. After a given time, the residual monomer was evaporated with a high vacuum pump. 2 ml of toluene were added to the residue and evaporated to insure complete removal of the monomer. This procedure was repeated three or four times until no residual TMSBD could be detected by 200 MHz^{1}H-NMR.

Cationic polymerization. Stock solutions containing 0.25 mol of initiator (I_2,$SnCl_4$ or tetracyanoethylene) per liter of dried toluene, and a saturated solution of Ph_3CSbCl_6 were prepared prior to the polymerization experiments. The glassware was dried by flame drying immediately before use.

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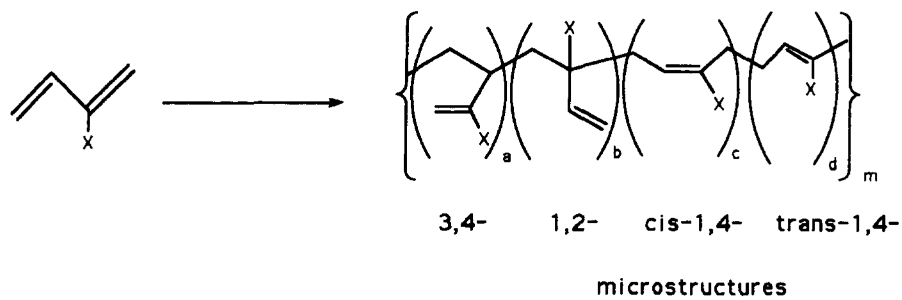

Fig. 1. Possible microstructures for the polybutadiene resulting from the polymerization of a 1,3-butadiene substituted on position 2 (do not take into account regioinsertion defects).

All experiments were carried out under argon. TMSBD (0.71 g, 5 mmol) and dried toluene (8 ml) were introduced into the flask. If the initiator was I_2, $SnCl_4$ or Ph_3CSbCl_6, the solution was refrigerated at −78° (for tetracyanoethylene, room temperature). The initiator (stock solution, 1 ml) was introduced and the solution was kept for 4 hr at the initial temperatures. The content of the flask was dropped into a large volume of phosphate buffer; no precipitation resulted. After decantation, the organic phase was evaporated and analyzed as described above.

(C) Characterization

GPC analyses were obtained using a Waters system including a pump Waters 510, a RI detector Waters 410, and four Waters Ultrastyragel columns (2 × linear, 2 × 1000 Å). THF was used as eluent and monodisperse polystyrene (Tosoh TSK) as standard.

^{1}H- and ^{13}C-NMR spectra were run on a Bruker AM500 spectrometer at 500.13 MHz (^{1}H) and 125.77 MHz (^{13}C) or with Varian VXR-200 and Gemini-200 spectrometers at 200 MHz (^{1}H) and 50.3 MHz (^{13}C), using 5 mm broadband probes. TMS signal was used as an internal reference for all spectra. $CDCl_3$ (99.8 atom % D) and C_6D_6 (99.5 atom % D) were purchased from Janssen Chimica.

A DEPT (Distorsionless Enhancement by Polarization Transfer) spectrum was used to differentiate C, CH, CH_2 and CH_3 ^{13}C NMR signals [7]. Unambiguous assignment was obtained using the two-dimensional proton-carbon heteronuclear chemical shift correlation spectroscopy. For the $^1J_{CH}$ connectivities, we assumed an average one bond carbon-proton coupling constant of about 139 Hz [fixed delay durations = $\Delta 1 = 1/2(^1J_{CH}) = 3.6$ msec; $\Delta 2 = 1/4(^1J_{CH}) = 1.8$ msec]. The two-dimensional data matrix was submitted to a Lorentz-Gauss transformation in

Table 1. Influence of temperature and AIBN concentration on the radical polymerization of TMSBD (bulk, 5 mmol)

Exp. No.	t (days)	T (°C)	AIBN mol%	C_6H_6 added (ml)	conv. (%)	%1,4	*cis/trans* 1,4	%3,4	M_w $\times 10^{-3}$*	M_n $\times 10^{-3}$*	M_w/M_n
1	9	45	5	1	28	77	0.71	23	3.9	2.5	1.5
					34	78	0.45	22			
2	5	60	5	0	52	83	0.61	17	5.9	3.9	1.5
					52	84	0.70	16			
3	5	60	5	1	47	84	0.90	16	4.3	2.4	1.7
					49	84	0.84	16			
4	5	60	24†	0	68	83	0.52	17	3.5	1.8	1.9
					68	83	0.56	17			
5	5	60	24	1	92	86	0.45	14	1.5	1.1	1.2
					94	85	0.52	15			
6	5	70	5	0	55	81	0.54	19	5.3	2.4	2.2
					56	81	0.47	19			
7	5	70	5	1	47	84	0.78	16	5.3	2.7	1.9
					51	83	0.63	17			
8	4	80	5	0	46	80	0.54	20	2.2	1.1	1.9
					47	82	0.62	18			
9	4	80	5	1	39	85	0.83	15	1.7	0.6	2.7
					39	84	0.71	16			
10	2	90	5	0	40	82	0.71	18	3.1	1.0	3.0
					44	86	0.62	14			
11	2	90	5	1	37	83	0.78	17	1.8	0.9	1.9
					38	85	0.85	15			

*Determined by GPC (polystyrene).
†Not entirely soluble.

Table 2. Experimental conditions investigated for the cationic polymerization of TMSBD; toluene: 8 ml, monomer: 5 mmol

T (°C)	Initiator	Amount of initator (mmol)
−78	Ph_3CSbCl_6	Saturated solution
−78	I_2	0,25
−78	$SnCl_4$	0,25
25	$(NC)_2C{=}C(CN)_2$	0,25

the t_1 dimension and to a sinusoidal multiplication in the t_2 dimension [7, 8], prior to Fourier transformation (power calculation mode).

RESULTS AND DISCUSSION

Radical polymerization

All polymerizations were carried out with azobis(isobutyronitrile) (AIBN) as initiator. Several conditions for reprecipitating poly(TMSBD) were investigated, but none of them proved to be effective. As a result, analysis of molecular weights and microstructures were performed on the residual material left after complete evaporation of volatiles (see Experimental Procedures).

Temperature is a factor known to largely influence the microstructure ratio in the radical polymerization of monomers like isoprene or chloroprene [9–13]. To test its influence on the radical polymerization of TMSBD, polymerizations in bulk were carried out at different temperatures (Table 1). Each experiment was achieved twice to check the reproducibility of the measurements, but GPC analysis were only performed on one of the samples. In most experiments, AIBN concentration was kept the same as in the literature (5 mol%). As AIBN is only partially soluble at 45° in neat TMSBD, a second set of experiments was performed with 1 ml of benzene as additive for 5 mmol of monomer; under these last conditions, AIBN was completely soluble in the full range of temperatures under investigation.

Analysis of Table 1 shows that the reaction temperature does not influence very much the microstructures ratio of the resulting poly(TMSBD): the 1,2-structure is never observed (see NMR Characterization) and the ratio between 1,4- and 3,4-structures is always very close of 82/18. This ratio is also practically independent on the presence or absence of benzene, and on the mole percentage of AIBN. These last two observations are quite logical, but the marginal influence of temperature seems surprising, although not completely unprecedented: isoprene for example exhibits a similar behavior with a 1,4/3,4/1,2-microstructures ratio being almost the same (90/5/5) for radical polymerization completed between -20 and 100° [10].

Cis/trans ratios for the two 1,4-structures range from 0.5 to 0.9. Due to overlapping of *cis* and *trans* vinylic peaks in ^{1}H-NMR, only a trend can be observed, indicating that the *trans* structure is always

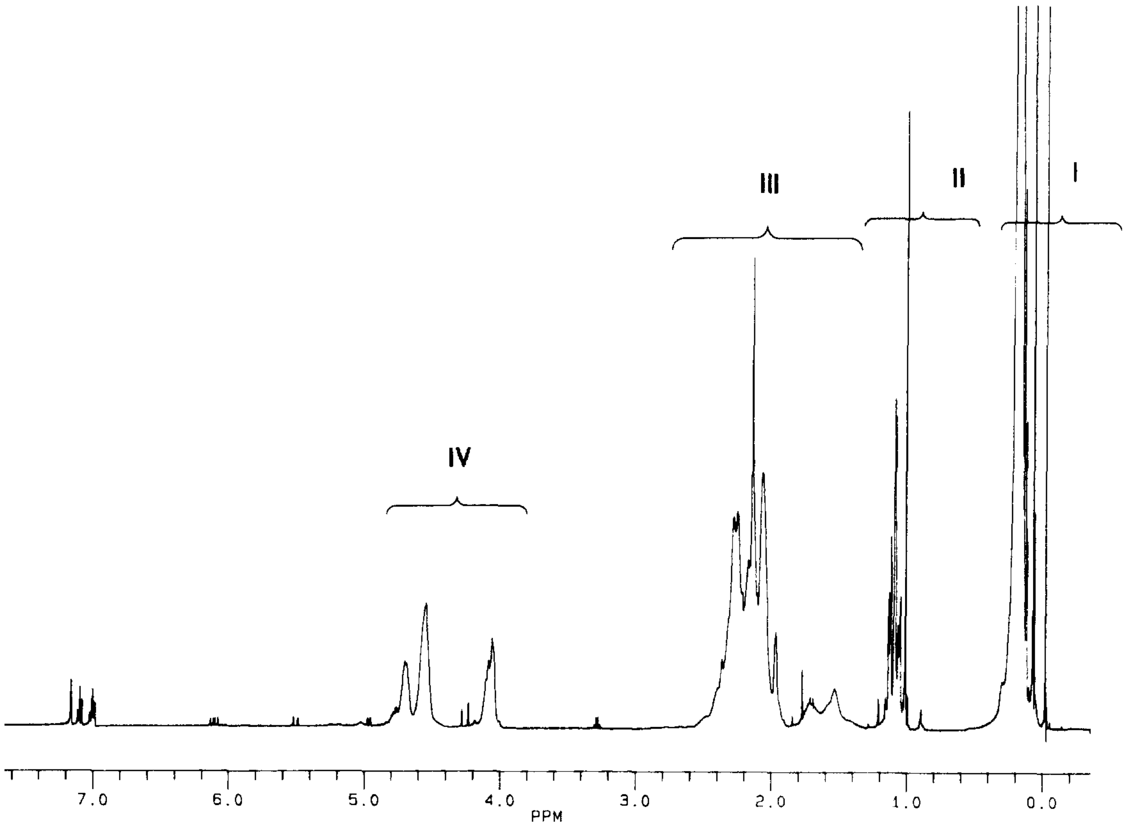

Fig. 2. 500 MHz ^{1}H-NMR spectrum of poly(TMSBD).

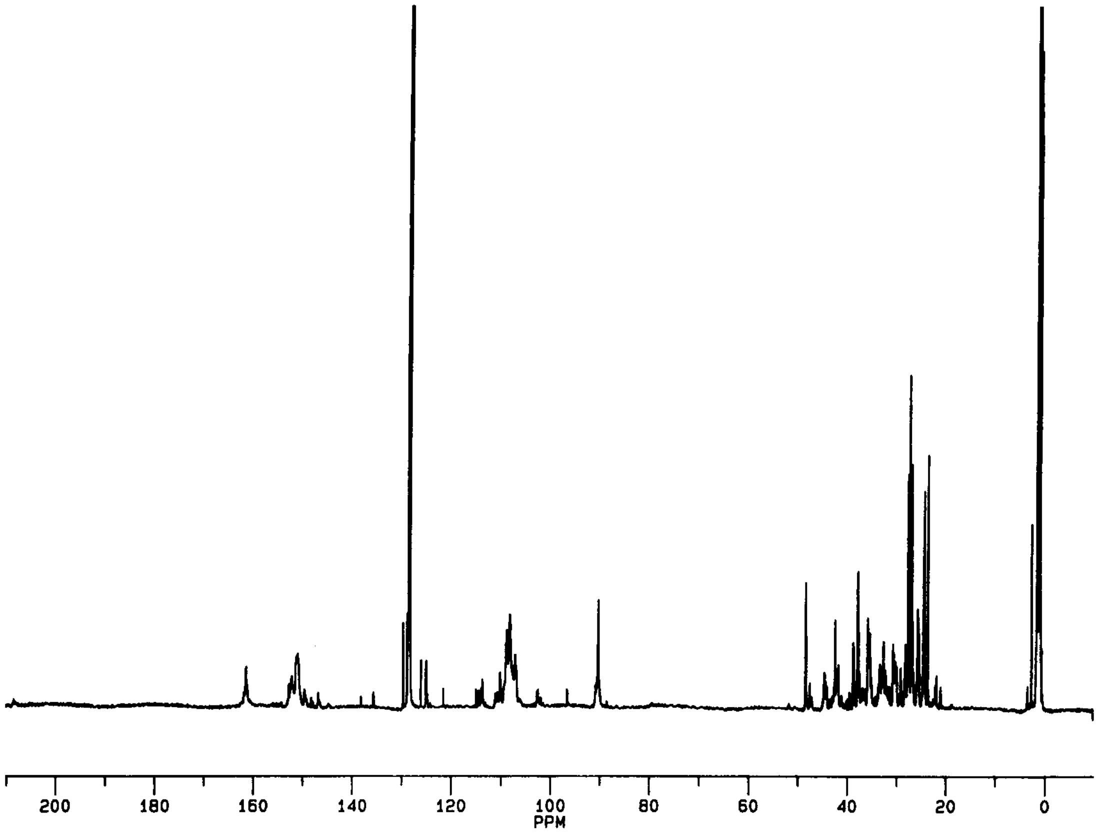

Fig. 3. 125.8 MHz ^{13}C spectrum of poly(TMSBD).

slightly preferred on the *cis* structure and is little affected by temperature.

Conversions obtained under the various conditions investigated follow the expected trends, i.e. rates increase with temperature and AIBN concentration. Experiments 4 and 5 seem to contradict this observation: dilution with benzene increases the conversion, all other conditions being the same. This apparent contradiction can be explained by the only partial solubility of the large amount of AIBN (24 mol %) introduced in TMSBD (exp 4); after the addition of 1 ml of benzene (exp. 5), AIBN was completely dissolved so that the real concentration of AIBN was actually higher in this experiment.

Molecular weights are low to moderate ($M_n > 10^4$) and decrease with increasing temperatures. Due to their low rate constants for radical propagation, low molecular weights are classically observed for butadienes polymerized under classical free-radical conditions [9–11]. Emulsion polymerization constitutes the normal solution to overcome the problem, but this possibility is not applicable to TMSBD due to its very poor hydrolytic stability.

Cationic polymerization

Since TMSBD is an electron rich butadiene, the action of some cationic initiators was investigated. These initiators were chosen on the basis of their known efficiency in the polymerization of trimethylsiloxyethene, a monomer structurally very close to TMSBD [14]. Table 2 summarizes the experimental conditions. Only $SnCl_4$ gave an oligomer with a very low molecular weight (GPC: $\bar{M}_n = 296$, $\bar{M}_w = 548$). The 200 MHz ^1H-NMR spectrum of this product was found to be very different from the spectra recorded for poly(TMSBD) samples resulting from radical polymerizations: in particular no vinylic proton was present.

NMR characterization of the polymer

^1H-NMR spectra of a poly(TMSBD) sample were recorded in different non-hygroscopic solvents. C_6D_6 was the solvent that afforded the best resolution between vinylic peaks; accordingly it was chosen as solvent for all subsequent NMR experiments. As an additional advantage deuterated benzene unlike $CDCl_3$ does not contain acid, and an acid-catalyzed desilylation of the polymer is expected to be very slow in this solvent.

One-dimension 500 MHz ^1H- and ^{13}C-NMR spectra are reproduced in Figs 2 and 3. As shown in Fig. 2, the ^1H-NMR spectrum can be schematically divided into four regions. Region 1 (0–0.5 ppm) corresponds to the Me_3Si protons, region II (0.9–1.2 ppm) to methyl groups of isobutyronitrile fragments, region III (1.3–2.6 ppm) to methylenic and methynic protons on the chain, and region IV (4.0–4.9 ppm) to vinylic protons. The isobutyronitrile fragments correspond both to end groups on the polymer and to low molecular weight products arising from the decomposition of AIBN.

The vinylic region includes four different peaks

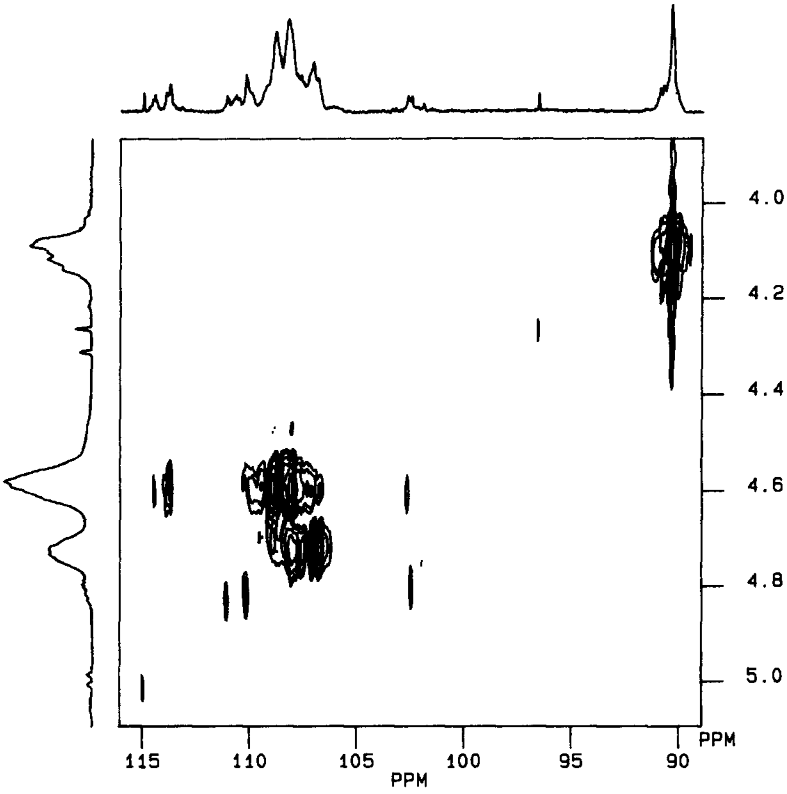

Fig. 4. Vinylic region of the ^{1}H-^{13}C correlation spectrum of poly(TMSBD).

centered at 4.07, 4.10, 4.58, and 4.72 ppm respectively. The ^{1}H–^{13}C correlation spectrum (Fig. 4) shows that protons in the 4.0–4.2 ppm region corresponds to carbons in the 89–91 ppm region and that protons in the 4.5–4.9 ppm region corresponds to carbons in the 102–115 ppm region. Finally, the DEPT spectrum

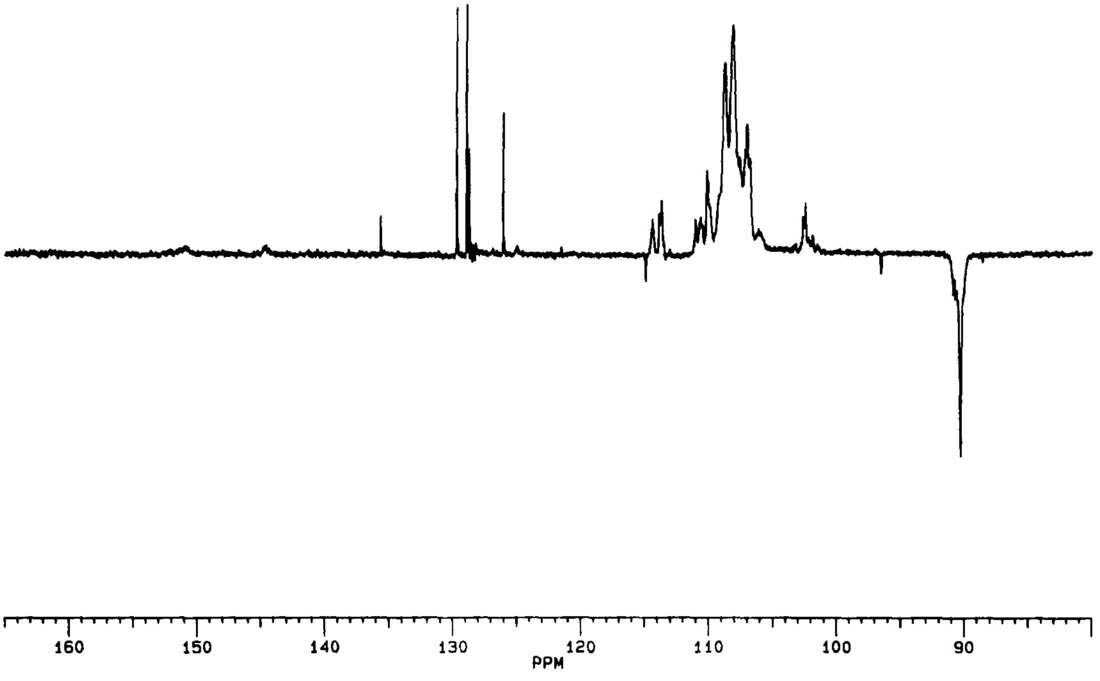

Fig. 5. Region corresponding to unsaturated carbons in the DEPT spectrum of poly(TMSBD).

(Fig. 5) leads to the conclusion that carbons included in the 89–91 ppm region are of CH_2-type and carbons in the 102–115 ppm region of CH-type. It thus appears that the previous putative assignment of the literature was correct: the two peaks centered at 4.72 and 4.58 ppm can be safely assigned to the *cis* and *trans*-1,4 microstructures, and peaks at 4.10 and 4.07 to the two protons of the 3,4-microstructure. The $H_2C{=}CH—$ structure that corresponds to the 1,2-microstructure does not appear on the spectrum (no signal at the expected positions for such protons, i.e. 5.0–6.0 ppm) and was not observed in any of the different polymers obtained during this study. The absence of 1,2-microstructure is confirmed by the lack of detection by DEPT for quaternary carbons in the 20–48 ppm region. By analogy with the known chemical shifts for the *E*- and *Z*-isomers of 5-trimethylsiloxy-4-nonene [15], we proposed to assign the proton centered at 4.58 ppm to the *trans*-1,4 microstructure and the proton centered at 4.72 ppm to the *cis*-1,4 microstructure.

In addition to this unambiguous assignment of the vinylic protons, the different spectra provides some additional valuable information:

(a) The ^{13}C spectrum shows a tiny peak at 209–210 ppm; this peak probably corresponds to a carbonyl group resulting from a partial hydrolytic desilylation of the polymer. Hexamethyldisiloxane, which is one of the product of the hydrolytic desilylation, also appears in the different spectra.

(b) On the ^{13}C spectrum, the 20–50 ppm region corresponds to the saturated carbons of the polymer chain. This region is partially overlapped between 23 and 29 ppm by the signals of the methyl carbons of the isobutyronitrile fragments. The DEPT spectrum shows that the ^{13}C signals in this region are mainly of the CH_2-type which would correspond to the saturated allylic carbons of the 1,4-microstructures and to one of the saturated carbon of the 3,4-microstructure. Finally, tertiary allylic carbon of the 3,4-microstructure can be found between 43 and 45 ppm.

(c) Vinylic carbons were found between 90 and 165 ppm. The DEPT spectrum allows to differentiate directly between $C{=}\underline{C}(OSiMe_3)R$, $C{=}\underline{C}HR$ and $H_2\underline{C} = C$ carbons. Accordingly, the peak centered at 161 ppm was assigned to the carbon substituted by the trimethylsiloxy group in the 3,4-structure and the peaks at 145–154 ppm to the carbons substituted by the trimethylsiloxy group in the 1,4-structures. Carbons unsubstituted by a trimethylsiloxy group and corresponding to the 1,4-structures have signals ranging from 101 to 115 ppm. A peak centered at 90 ppm corresponds to the $H_2C{=}$ carbon of the 3,4-structure.

CONCLUSION

Radical polymerization of 2-(trimethylsiloxybutadiene) under different experimental conditions yielded a polymer of low to moderate molecular weights. The microstructure of the resulting polybutadiene was analyzed by NMR: *cis*- and *trans*-1,4-microstructures and 3,4-microstructure were observed in all cases, but in no case was 1,2-microstructure detected. The evolution of microstructure ratios and molecular weights with temperature was also investigated. Finally, attempts to polymerize the diene in the presence of cationic initiators described as efficient for trimethylsiloxyethene proved unsuccessful.

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