Solvent-induced allylic rearrangements in poly(trichlorobutadiene) chains

T. L. Lebedeva,[a] I. I. Vointseva,[b] L. M. Gil'man,[b] P. V. Petrovskii,[b] and T. A. Larina[b]*

[a]A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 117912 Moscow, Russian Federation. Fax: 007 (095) 230 2224

[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: 007 (095) 135 5085. E-mail: DIR@INEOS.AC.RU

It was established by Fourier-transform IR and ^{1}H NMR spectroscopy that a portion of the units of poly(1,1,2- and 1,2,3-trichlorobuta-1,3-diene) chains rearrange with migration of the allylic chlorine (1—4%) and allylic hydrogen (3—10%) under the influence of chloroform. Rearrangement with the migration of hydrogen under the influence of $CDCl_3$, CCl_4, and THF was also observed.

Key words: poly(trichlorobutadiene), allylic rearrangement.

In studies of the structure of the products of chemical transformations of poly(1,1,2-trichlorobuta-1,3-diene) (1,1,2-PTCB), some features have been found that indicated that a rearrangement in the chain of this polymer occurred resulting in the migration of the allylic chlorine.[1,2] However, the questions of when and how the rearrangement occurs (at the moment of dissolution under the influence of the solvent or in the course of the reaction under the action of a reagent) as well as the problem of a possible rearrangement with migration of the allylic hydrogen have remained open. The answers to these questions are of importance in the studies of the structure and chemical transformations of not only 1,1,2-PTCB, but also of other chloro derivatives of polychloroprene.

The aim of the present work was to study the allylic rearrangements in 1,1,2-PTCB under the action of solvents of different nature and polarity as well as the effect of the conditions of the synthesis of the polymer on its ability to rearrange. Poly(1,2,3-trichlorobuta-1,3-diene) (1,2,3-PTCB), whose synthesis and structure have not been studied before, was selected as a model for comparison.

Experimental

1,1,2-PTCB and 1,2,3-PTCB were obtained by radical polymerization of the corresponding monomers in emulsion (1,1,2-PTCB$_e$ and 1,2,3-PTCB$_e$) and in bulk (1,1,2-PTCB$_b$ and 1,2,3-PTCB$_b$). Polymerizations of the monomers in aqueous emulsion were conducted in the presence of an initiator (0.1 mol.% of $K_2S_2O_8$) at +50 °C for 10 h; those in bulk were conducted without initiator at −10 °C for 4 months. All the polymers were completely soluble in aromatic and chlorinated hydrocarbons, dioxane, and THF; the yields were ~75—80%; the characteristics of the polymers are given in Table 1.

The fractional precipitation of 1,1,2-PTCB$_e$ with methanol from benzene at 25 °C gave 13 fractions. The intrinsic viscosities ([η]) of the fractions and of non-fractionated polymers were measured on an Ubbelohde viscosimeter in benzene at 25 °C. The weight-average molecular weights (M_w) were calculated from the data of angular light scattering by double extrapolation to zero angle and zero concentration using the formula

$$M_w = [KC/R_\theta]^{-1}{}_{\theta=0},$$

where $K = (2\pi^2 n_0^2/N_A\lambda_0^4)\cdot(dn/dC)^2$; C is concentration, g mL^{-1}; n_0 is the refractive index of benzene; $dn/dC = 0.110$ is

Table 1. Characteristics of the polymers obtained in bulk and in emulsion

Polymer	Cl content (%)*	[η] /dL g^{-1}	$M_w \cdot 10^{-3}$ (light scattering)	$M_w \cdot 10^{-3}$ (GPC)	$M_n \cdot 10^{-3}$ (GPC)	M_w/M_n (GPC)
1,1,2-PTCB$_e$	67.41	0.74	550.5	600.0	80.0	7.5
1,1,2-PTCB$_b$	66.62	0.90	1300.0	1500.0	180.0	8.3
1,2,3-PTCB$_e$	66.98	0.29	87.0**	100.0	20.0	5.0
1,2,3-PTCB$_b$	67.51	0.16	37.0**	—	—	—

* Calculated: 67.57. ** M_w was measured at the angle of 90°.

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 4, pp. 763—768, April, 1997.

1066-5285/97/4604-0732 $18.00

the increment of the refractive index of the polymer dissolved in benzene; R_θ is the excess angular light scattering by the solution of given concentration; θ is the scattering angle; N_A is the Avogadro number; λ_0 is the wavelength of the incident light.

In addition, the molecular weight characteristics of the polymers were determined by gel-permeation chromatography (GPC) using a Waters 150-C high-temperature liquid chromatograph (Styragel of pore size 500, 10^3, and 10^5 Å as the packing; calibration against Waters polystyrene standards in the range of molecular weights from $3.5 \cdot 10^3$ to $2.7 \cdot 10^6$).

The IR spectra of the polymers were recorded on a Bruker IFS-113V spectrometer. The samples were prepared as cast films on silicon plates by evaporation of solvents from 2% solutions of the polymers. Solvents of UV spectroscopic grade (dioxane, chloroform, chloroform-d, benzene, nitrobenzene, CCl_4, THF, and 1,2-dichloroethane) were used.

The ^{1}H NMR spectra of the polymers were recorded on a Bruker AMX-400 spectrometer (400.13 MHz). The samples were prepared as 10% solutions in chloroform-d ($\delta(CHCl_3)$ = 7.25).

Table 2. Molecular weight characteristics of the fractions of 1,1,2-PTCB$_e$

Fraction number	$[\eta]$ /dL g^{-1}	$M_w \cdot 10^{-3}$ (light scattering)	$M_w \cdot 10^{-3}$ (GPC)	$M_n \cdot 10^{-3}$ (GPC)	M_w/M_n (GPC)
1	0.13	—	32.0	12.0	2.6
2	0.18	—	52.0	15.0	3.5
3	0.26	100.0	98.0	26.0	3.7
4	0.27	—	113.0	28.0	4.0
5	0.30	—	123.9	28.3	3.7
6	0.34	—	152.0	33.0	4.7
7	0.35	—	154.0	58.0	2.6
8	0.45	220.0	225.0	90.0	2.5
9	0.50	—	300.0	120.0	2.5
10	0.61	344.8	—	—	—
11	0.88	740.0	738.4	312.5	4.0
12	1.00	869.0	—	—	—
13	1.10	—	822.0	334.0	2.5
*14**	0.74	550.5	600.0	80.0	7.5

* The original (non-fractionated) polymer.

Results and Discussion

Under the conditions selected, 1,1,2- and 1,2,3-trichlorobuta-1,3-diene are readily polymerized according to a radical mechanism both in bulk and in emulsion with the formation of high-molecular-weight soluble polymers in high yields.

As can be seen from the data of Table 1, 1,1,2-PTCB$_b$ has a higher M and a higher polydispersity index (M_w/M_n) than 1,1,2-PTCB$_e$.

It was shown using the GPC and angular light scattering techniques that the dependence of $\log[\eta]$ on $\log M_w$ for the fractions of 1,1,2-PTCB$_e$ is linear over a wide range of M_w (Fig. 1).

The coefficients K and a in the Mark—Kuhn—Houwink equation for 1,1,2-PTCB have been determined previously[3] by the method of light scattering at the angle of 90°. However, 1,1,2-PTCB has a high M, whose true value can only be determined by using the method of angular light scattering. We have obtained the following equation:

$$[\eta] = 1.684 \cdot 10^{-4} \cdot M^{0.64} \text{ (benzene, 25 °C).} \quad (1)$$

A number of facts have been found that might give grounds to suggest the appearance of a considerable number of branchings in the macromolecules of 1,1,2-PTCB: the non-fractionated polymers as well as fractions of 1,1,2-PTCB$_e$ have high polydispersity indices (Tables 1 and 2); the shape of the Zimm diagram for the non-fractionated polymers is somewhat convex (for instance, Fig. 2, *a*).

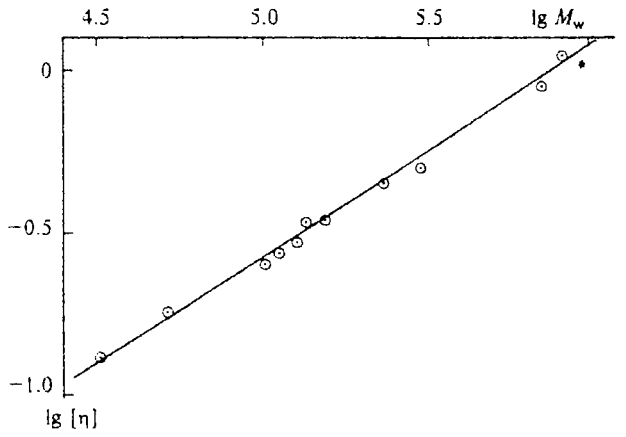


Fig. 1. Dependence of $\log[\eta]$ on $\log M_w$ for fractions of 1,1,2-PTCB$_e$ (benzene, 25 °C); non-fractionated sample is marked by an asterisk.

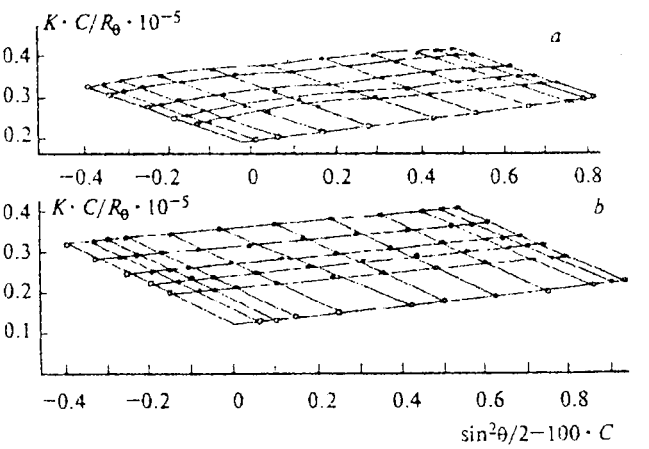


Fig. 2. Zimm diagrams for the samples of 1,1,2-PTCB$_e$: non-fractionated polymer (*a*); fraction No. *13* in Table 2 (*b*).

Table 3. Chemical shifts (δ) of individual groups in the isomers of PTCB

Group	1,1,2-PTCB unit		1,2,3-PTCB unit	
	~CCl_2—[CH_2>C=C<Cl, H, CCl_2]—CH_2~	(1)	~CHCl—[CH_2>C=C<Cl, Cl, CHCl]—CH_2~	(1a)
—CH_2—	3.50		3.10; 3.38	
—CH=	6.61		—	
—CH—	—		5.68	
	~CH_2—[CH_2>C=C<Cl, H, CCl_2]~	(2)	~CH_2—[CH_2>C=C<Cl, Cl, CHCl]~	(2a)
—CH_2—	2.56		2.92	
—CH=	6.75		—	
—CH—	—		5.39	
	~CCl_2—[CH_2 CH=CCl, CCl_2]~	(3)	—	
—CH=	6.44		—	
	~[CH_2—CH(CCl=CCl_2)]~	(4)	~[CH_2—CCl(CCl=CHCl)]~	(4a)
—CH_2—	1.90		1.90	
=CH—	—		2.60	
—CH—	3.00		—	
	~[CH_2—CHCl—CCl=CCl]~	(5)	~[CH_2—CCl_2—CCl=CH]~	(5a)
—CH_2—	3.20; 3.40		3.50	
—CH=	—		6.61	
—CH—	6.10		—	
	~[CH=CH—CHCl—CCl_2]~	(6)	~[CHCl—CH=CCl—CHCl]~	(6a)
—CH=	6.90; 7.10		7.10	
—CH—	4.64		5.53	

However, the obtained value of the coefficient a in Eq. (1) ($a > 0.5$), the linear dependence of $\log[\eta]$ on $\log M_w$ over a wide range of M_w (from 30000 to 900000), and the classical shape of the Zimm diagram even for the highest-molecular-weight fraction of 1,1,2-$PTCB_e$ (Fig. 2, *b*) are evidence for the linear structure of the polymer macromolecules.

The convex shape of the Zimm diagrams of the non-fractionated polymers is most probably associated with their high polydispersity rather than with their branching, which is also confirmed by the presence of a long high-molecular tail on the curve of molecular weight distribution for 1,1,2-$PTCB_e$.

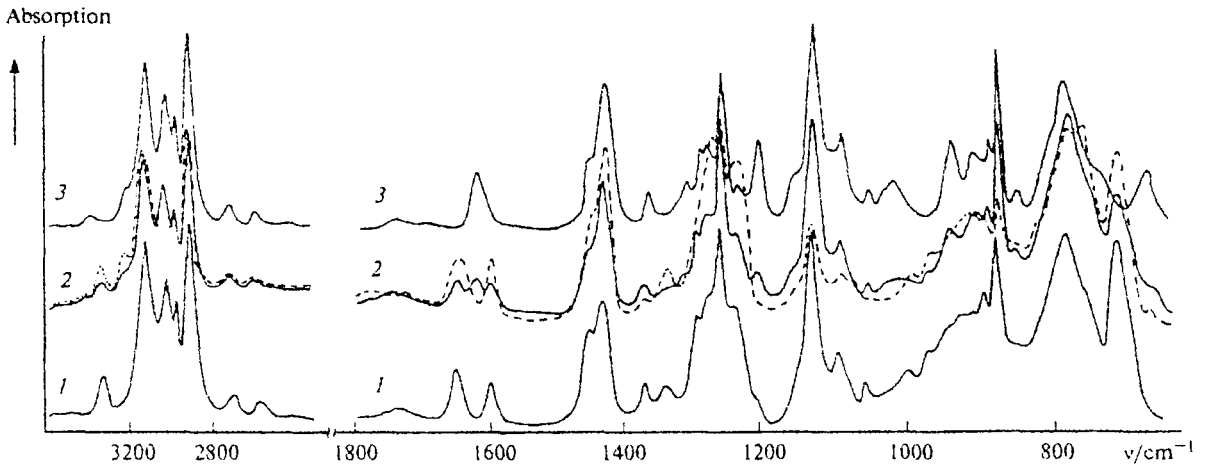


Fig. 3. FT-IR spectra of the polymers: *1*, 1,1,2-$PTCB_e$ and 1,1,2-$PTCB_b$ in dioxane (both polymers have identical spectra); *2*, 1,1,2-$PTCB_e$ (solid line) and 1,1,2-$PTCB_b$ (dashed line) in chloroform; *3*, 1,2,3-$PTCB_b$ in dioxane.

Table 4. Absorption band frequencies in the FT-IR spectra of PTCB (ν/cm^{-1})

Calculation[6]		Experiment		
1,1,2-PTCB	1,1,2-$PTCB_b$; 1,1,2-$PTCB_c$ (in dioxane)	1,1,2-$PTCB_c$ (in chloroform)	1,1,2-$PTCB_b$ (in chloroform)	1,2,3-$PTCB_b$ (in dioxane)
3030 *trans*	3066	3065	3066	3098
3028 *cis*		3057		
		3002	3017	3004
	2960*	2960*	2961*	2961*
2910	2913*	2914*	2918*	2913*
	2888*	2888*	2888*	2888*
2858	2854*	2854*	2855*	2854*
	2750	2752	2751	2751
	2692	2693	2711	2693
	1738	1740	1744	1742
1654 *trans*	1646	1645	1646	
1645 *cis*		1618		1620
	1595	1596	1596	
	1452	1452	1452	1452
	1445	1445	1443	
1439	1426	1426	1426	1426
1340 *trans*	1365	1364	1365	1364
1332 *cis*	1333	1324	1332	
		1304		1306
1286 *cis*	1287	1287		1288
1270 *trans*	1272	1272	1267	1276
1236 *cis*	1254	1254	1255	1254
1230 *trans*	1234	1231	1231	1230
		1200	1200	1200
1152 *trans*		1149	1149	
1132 *cis*	1123	1122	1123	1122
1121 *trans*	1083	1083	1082	1083
1040 *cis*	1048	1048	1060	1048
1033 *trans*		1013	1047	1016
	989		987	
959 *cis*	961	961	961	
928 *trans*	937	937	937	937
	916	916	916	
	901	902	901	905
	888	888	888	888
	875	875	874	875
825 *cis*		850	851	850
781 *trans*	782	782	780	787
765	sh	sh	759	sh
710 *cis*	711	714	714	
675 *trans*; 664 *cis*		675	670	675

* The resonance effect of splitting of the bands of stretching vibrations of the CH_2 group in the $-CH_2-C=C-$ fragment.[7]

A comparison of 1,1,2-PTCB and 1,2,3-PTCB shows that the former has a higher molecular weight and a larger value of the polydispersity index than the latter, when the polymerization of the corresponding monomers is carried out under identical conditions (see Table 1). The M_w value for 1,2,3-PTCB determined by two independent procedures does not fit the dependence of $\log[\eta]$ on $\log M_w$ for 1,1,2-PTCB shown in Fig. 1, *i.e.*, Eq. (1) is not valid for this polymer.

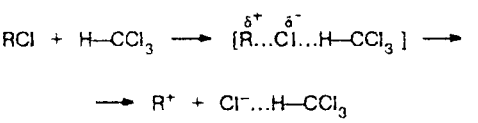
It has been established previously[4,5] by IR and NMR spectroscopy that 1,1,2-$PTCB_c$ consists mainly of 1,4-*trans*-units of normal ("head-to-tail" type) addition (structure **1** in Table 3, the corresponding $\nu(C=C)$ is at 1654 cm^{-1}). Also, 1,4-units of anomalous addition (structure **2**), 1,4-*cis*-units (structure **3**, $\nu(C=C)$ 1645 cm^{-1}), and 3,4-units (structure **4**, $\nu(C=C)$ 1600 cm^{-1}) were found in the polymer structure. A theoretical analysis of the vibrational spectra of the *cis*- and *trans*-isomers of 1,1,2-PTCB has also been carried out[6] (these data are listed in Table 4).

One could expect that the topological structures of the specimens of 1,1,2-PTCB obtained under substantially different conditions of polymerization would also be different. However, the analysis of the FT-IR spectra of solutions of 1,1,2-$PTCB_c$ and 1,1,2-$PTCB_b$ in dioxane (an aprotic, non-polar solvent with $\mu = 0$ and $\varepsilon = 2.21$) showed that they virtually coincide (spectrum *1* in Fig. 3). Hence, in this case both specimens have the identical topological structure, which is formed in the course of the radical polymerization of the monomer.

The spectra of solutions of these polymers in chloroform ($\mu = 1.06$ and $\varepsilon = 4.72$), which specifically solvates the chlorine atoms in the chlorine-containing polymers,[8] appreciably differ from one another and from the spectra of solutions in dioxane (spectrum *2* in Fig. 3).

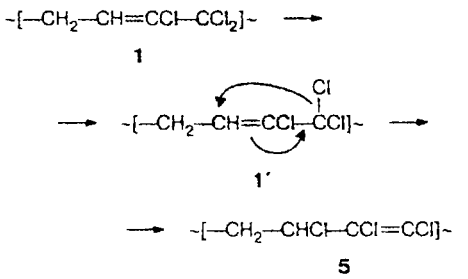
The specific solvation of a halogen by chloroform in a transition state is known[8] to be the driving force in the heterolytic cleavage of the C—Cl bonds in alkyl halides (Scheme 1).

Scheme 1



We believe that chloroform induces an allylic rearrangement with migration of chlorine in 1,1,2-PTCB (Scheme 2).

Scheme 2



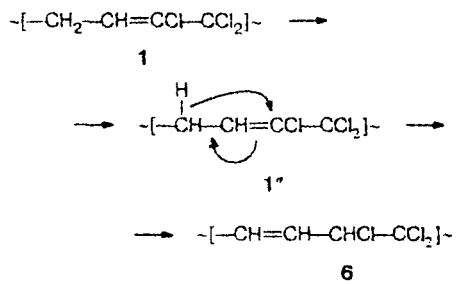
In this case, the [—CCl=CCl—] and [—CHCl—] groups must appear instead of the [—CH=CCl—] and [—CCl_2—] groups, *i.e.*, 1,1,2-PTCB partly transforms into 1,2,3-PTCB (structure **1a** in Table 3).

Actually, the bands at 3066 and 1646 cm^{-1}, which are characteristic of the [—CCl=CH—] group[6,9] and the band at 714 cm^{-1} (corresponding to the [—CCl_2—] group[10—12]) in the IR spectrum of the solution of 1,1,2-$PTCB_e$ in chloroform (spectrum *2* in Fig. 3, solid line) are less intense than those in the spectrum of its solution in dioxane (spectrum *1* in Fig. 3). In addition, spectrum *2* contains bands at 3002 and 675 cm^{-1}, which are characteristic of the [—CHCl—] group incorporated in the [—CH_2—CHCl—CCl=] fragment,[10,11] and a band at 1618 cm^{-1} corresponding to the [—CCl=CCl—] group.[10]

To confirm the assignments made, we investigated the IR spectrum of a solution of 1,2,3-$PTCB_b$ in dioxane (spectrum *3* in Fig. 3). The frequencies of the most characteristic lines in this spectrum (3004, 1620, and 675 cm^{-1}) nearly coincide with those in the spectrum of a solution of 1,1,2-$PTCB_e$ in chloroform (Table 4). Hence, rearrangement with migration of the allylic chlorine does occur in 1,1,2-$PTCB_e$ under the action of chloroform.

An analysis of the spectrum of a solution of 1,1,2-$PTCB_b$ in chloroform allows us to draw the conclusion that allylic rearrangement occurs in this polymer as well, but in this case, with migration of proton (Scheme 3).

Scheme 3



The intensities of the bands characteristic of the [—CH_2—] group (1123, 888, and 875 cm^{-1}) decrease in the spectrum of the solution of 1,1,2-$PTCB_b$ in chloroform (spectrum *2* in Fig. 3, dotted line). Simultaneously, the intensities of the bands corresponding to a [=CH—] group containing a Cl atom at the α-position (1267 and 759 cm^{-1}) increase and bands at 3017 and 675 cm^{-1} appear, which correspond to the [—CHCl—] group incorporated in the [=CH—CHCl—CCl_2—] fragment.

Note that allylic rearrangements occur in 1,2,3-PTCB in chloroform as well, however, in this case (according to IR spectroscopy) the rearrangement with migration of the hydrogen atom is dominant.

^{1}H NMR analysis of 1,1,2-PTCB and 1,2,3-PTCB confirmed the conclusion drawn on the basis of the analysis of the IR spectra that the chloroform-induced allylic rearrangements in PTCB involve both the chlorine and the hydrogen atoms.

In addition to the signals corresponding to the previously identified structures **1**—**4**, the ^{1}H NMR spectrum of 1,1,2-PTCB contains unidentified weak signals at δ 3.20 and 3.40 (see Table 3). As can be seen from Table 3, these signals are characteristic of the [—CH_2—] group in the spectrum of 1,2,3-PTCB (**1a**), in which they correspond to the dominating 1,4-units and have a very high intensity. Therefore, we assigned these signals in the spectrum of 1,1,2-PTCB to the analogous groups formed in 1,4-units as a result of the allylic chlorine migration (structure **5**).

In turn, very weak signals at δ 3.50 and 6.61 were found in the ^{1}H NMR spectrum of 1,2,3-PTCB. We assigned them to the [—CH_2—] and [—CH=] groups in structure **5a**, respectively (rearrangement of 1,4-units with allylic chlorine migration). These signals have high intensities in the spectrum of 1,1,2-PTCB (structure **1**).

Rearrangements with migration of the allylic hydrogen resulting in the formation of structures **6** and **6a** in the polymers are detected by the appearance of one (in the case of 1,2,3-PTCB) or two (in the case of 1,1,2-PTCB) weak signals from the [—CH=] group in the spectra in the region of δ 7. In addition, weak signals at δ 4.64 or 5.53 corresponding to the [—CHCl—] group appear in the spectra of these polymers (the latter assignment was made by analogy with the signals in the region of δ 4.61—5.03 in the spectrum of polymer ~[CCl_2—CHCl—CHCl]~[13]).

The data obtained from the ^{1}H NMR spectra allowed us to calculate the percentage of anomalous units that are formed in the course of the synthesis of the polymers and the percentage of rearranged units formed under the action of chloroform-d for each of the polymers (Table 5). As can be seen, 1,4-*trans*-units (**1**, **2** and **1a**, **2a**) are mostly formed in the polymerization of the monomers. The percentage of anomalous 3,4-units (**4**) in 1,1,2-PTCB is ~6% regardless of the method of polymer synthesis; their content in 1,2,3-PTCB is negligible (**4a**).

Table 5. Content of units (%) with different structures in the isomers of PTCB (according to ^{1}H NMR in $CDCl_3$)

Unit structure	Unit	1,1,2-$PTCB_e$	1,1,2-$PTCB_b$	Unit	1,2,3-PTCB*
1,4-*trans*-	**1+2**	79	70	**1a+2a**	96
1,4-*cis*-	**3**	12	10	—	—
3,4-	**4**	6	6	**4a**	<0.5
1,4- with migration of Cl	**5**	3	4	**5a**	1
1,4- with migration of H	**6**	—	10	**6a**	3

* 1,2,3-$PTCB_b$ and 1,2,3-$PTCB_e$ have identical structure.

The percentage of anomalous 1,4-units (**2** and **2a**) ("head-to-head" addition) is ~20% in 1,1,2-PTCB and ~10% in 1,2,3-PTCB (regardless of the procedure used to obtain the polymers).

cis-1,4-Units (**3**) were found in 1,1,2-PTCB, their percentage (10—12%) was virtually independent of the method of synthesis of the polymer. These units were not detected in 1,2,3-PTCB.

The percentage of 1,4-units (**5** and **5a**) rearranged with migration of the allylic chlorine is 1—4%. However, judging from the IR spectra, $CHCl_3$-induced rearrangement occurs to a much greater extent than that under the action of $CDCl_3$. The rearrangement with the migration of chlorine is somewhat more characteristic of 1,1,2-PTCB; likely, steric and electrostatic hindrances in 1,2,3-PTCB hamper the interaction of Cl^- with a carbocation already bearing $Cl^{\delta-}$.

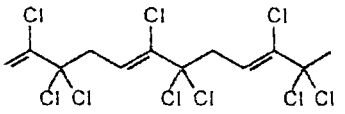
The rearrangement with migration of hydrogen (**6** and **6a**) is most characteristic of 1,1,2-$PTCB_b$; it has not been observed in 1,1,2-$PTCB_e$.

Thus, the results of this investigation show that 1,1,2-PTCB is more susceptible to allylic rearrangements than 1,2,3-PTCB, *i.e.*, carbonium ions **1'** and **1"** from 1,1,2-PTCB are apparently more stable than the corresponding carbonium ions from 1,2,3-PTCB. Moreover, the results obtained, which show that allylic rearrangement with the migration of hydrogen predominates in both polymers, allows one to assume that type **1"** chloroallylic carbanions are more stable than the corresponding type **1'** carbocations. This is consistent with theoretical concepts based on the inductive effect of the chlorine atoms in chloroallylic radicals.[14]

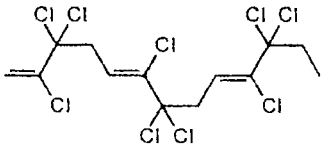
It was also found that allylic rearrangement with migration of hydrogen occurs under the action of CCl_4 and THF. Attempts to detect allylic rearrangement with migration of chlorine under the action of CCl_4, 1,2-dichloroethane, THF, benzene, and nitrobenzene using FT-IR spectroscopy have failed.

One can assume that the different ability of poly(trichlorobutadienes) to undergo allylic rearrangements is determined by their conformation. As can be seen from Table 5, the chemical structure of 1,1,2-PTCB (the content of 3,4- and 1,4-*cis*-units) is hardly affected by the conditions of the synthesis. However, the set of conformers of 1,4-*trans*-units can be different (for instance, **7**—**9**).

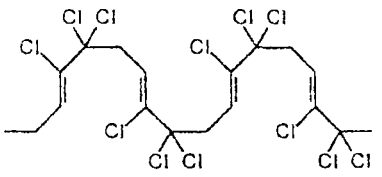
These conformers are spectroscopically indistinguishable, but they should differ in their hydrodynamic properties. In fact, according to the data of angular light scattering, the root-mean-square radius of gyration for 1,1,2-$PTCB_b$ is substantially smaller than that for 1,1,2-$PTCB_e$ (184 and 277 Å, respectively). In addition, the experimental value of $[\eta]$ for 1,1,2-$PTCB_b$ (see Table 1) is much lower than that calculated using formula (1) (1.25 dL g^{-1}), even with allowance for polydispersity, whereas the $[\eta]$ value obtained for 1,1,2-$PTCB_e$ is in reasonably good agreement with that calculated using formula (1) (see Fig. 1).



7



8



9

It seems likely that the proportion of the energetically most favorable conformation **7** (*trans*-zigzag),[15] in which allylic chlorine and hydrogen can migrate, increases in the slow spontaneous polymerization of the monomer at low temperatures (synthesis of 1,1,2-$PTCB_b$). Fast polymerization of the monomer at elevated temperatures (synthesis of 1,1,2-$PTCB_e$) most likely results in an array of random conformations of the types **8** or **9** with intramolecular dipole-dipole interactions and steric hindrances hampering the allylic rearrangements, most of all migration of hydrogen.

The authors express their sincere gratitude to N. A. Papazyan for preparing 1,2,3-trichlorobutadiene, and to G. A. Otradina for determining the molecular weights of the polymers by GPC.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 94-03-0804).

References

1. I. I. Vointseva, A. S. Shashkov, F. K. Velichko, and A. P. Suprun, *Vysokomol. Soedin., Ser. A*, 1979, **21**, 1625 [*Polym. Sci. USSR*, 1979, **21** (Engl. Transl.)].
2. I. I. Vointseva, A. S. Shashkov, and A. P. Suprun, *Vysokomol. Soedin., Ser. A*, 1978, **20**, 1640 [*Polym. Sci. USSR*, 1978, **20** (Engl. Transl.)].
3. T. A. Soboleva, A. P. Suprun, and S. A. Pavlova, *Vysokomol. Soedin.*, 1964, **6**, 89 [*Polym. Sci. USSR*, 1964, **6** (Engl. Transl.)].
4. Yu. G. Gololobov, N. V. Klimentova, and K. A. Mager, *Vysokomol. Soedin., Ser. A*, 1987, **29**, 2367 [*Polym. Sci. USSR*, 1987, **29** (Engl. Transl.)].

5. P. V. Petrovskii, N. V. Klimentova, K. A. Mager, G. A. Niazashvili, and Yu. G. Gololobov, *Vysokomol. Soedin., Ser. B*, 1991, **32**, 625 [*Polym. Sci. USSR*, 1991, **32** (Engl. Transl.)].
6. V. L. Kofman, O. I. Kondratov, and L. A. Gribov, *Zh. Prikl. Spektrosk.*, 1981, **34**, 456 [*Russ. J. Appl. Spectr.*, 1981, **34** (Engl. Transl.)].
7. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., London, 1954.
8. B. A. Chubar, *Usp. Khim.*, 1965, **34**, 1227 [*Russ. Chem. Rev.*, 1965, **34** (Engl. Transl.)].
9. A. R. Prabakaran and D. S. Smohan, *Proc. Ind. Nat. Sci. Acad.*, 1991, **57**, 553.
10. A. Yu. Kolesnitskaya, N. A. Artyushkina, G. M. Kuramshina, and Yu. A. Pentin, *Zh. Fiz. Khim.*, 1993, **67**, 113 [*Russ. J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
11. B. V. Lopatin, V. G. Vinokurov, N. B. Lopatina, and V. A. Berdyugin, *Zh. Prikl. Spektrosk.*, 1991, **55**, 392 [*Russ. J. Appl. Spectr.*, 1991, **55** (Engl. Transl.)].
12. S. H. Chough and S. Krimm, *Spectrochim. Acta, A*, 1990, **46**, 1419.
13. A. P. Suprun, A. S. Shashkov, T. A. Soboleva, G. K. Semin, T. T. Vasil'eva, G. P. Lopatina, T. A. Babushkina, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, 1967, **173**, 356 [*Dokl. Chem.*, 1967, **173** (Engl. Transl.)].
14. T. I. Temnikova, *Kurs teoreticheskikh osnov organicheskoi khimii* [*Fundamentals of Organic Chemistry*], Khimiya, Leningrad, 1968, 1006 pp. (in Russian).
15. H. Morawetz, in *Macromolecules in Solution*, Interscience, New York, 1965.

Received September 19, 1996