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Poly(1,1,2-TrichlorobutadJene-1,3) and its Compositions: Part I—Synthesis, Structure and Reactivity

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Poly(1,1,2-Trichlorobutadiene-1,3) and its Compositions: Part I—Synthesis, Structure and Reactivity

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(Received February 15, 1993)

Studies of the radical polymerization and copolymerization of 1,1,2-trichlorobutadiene-1,3 with various unsaturated compounds are reviewed. The physicochemical properties and chemical reactions of 1,1,2-trichlorobutadiene-1,3 as well as its ability for chemical interaction with low-molecular and high-molecular compounds are described.

KEY WORDS 1,1,2-trichlorobutadiene-1,3, polymerization, copolymerization, chemical reactivity, elastomers, adhesives.

INTRODUCTION

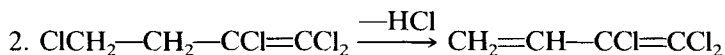
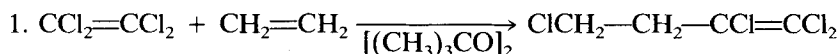
One of numerous chloroderivatives of butadiene—poly(1,1,2-trichlorobutadiene-1,3) (PTCB)—attracted a special attention of investigators because of its high adhesiveness, namely its capability to bond various materials. PTCB is, therefore, one of the most promising adhesives for bonding rubbers to one another and rubbers to metals. In addition, PTCB attracted attention because of its high reactivity and potential for a variety of interpolymer reactions.

The presence of highly mobile allyl chlorine atoms in the PTCB structure opens up possibilities of its chemical modification and obtaining of polymers with complexes of beneficial properties. Thus, an interaction of PTCB with amines results in production of electrical-conducting, film-forming polymers with satisfactory strength characteristics. PTCB is usable for fixation of water-soluble polyamines with bactericidal properties on various surfaces. This offers scope for obtaining bactericidal antifouling coatings, stable in aqueous and aggressive media. High reactivity of PTCB in interpolymer reactions makes possible its use as a polymer linkage between two polymers that do not react to one another.

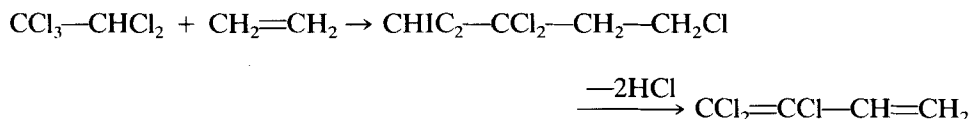
PTCB contains chlorine (67%) in its structure and imparts a fire resistance and an increased adhesion to compositions based on this polymer.

1. SYNTHESIS OF THE MONOMER

Scientists of the Institute of Organo-Element Compounds under the direction of academician A. N. Nesmeyanov were the first to synthesize 1,1,2-trichlorobutadiene-1,3 (TCB) in 1958.^{1,2} A. B. Belyavskii obtained TCB by telomerization of ethylene with tetrachloroethylene under 50–200 atm. pressure in the presence of peroxides. From the mixture of telomerization products he isolated by fractionation 1,1,2,4-tetrachlorobutene-1 (20% yield); then this product produced TCB with 70% yield on dehydrochlorination by alcohol alkali. The reaction proceeds via the scheme:



Belyavskii *et al.* proposed³ a more convenient method for synthesis of polychlorinated dienes including TCB, by telomerization of unsaturated compounds with pentachloroethane in the presence of iron pentacarbonyl. The reaction proceeds in isopropyl alcohol medium at 130–140°C, and polychloroalkanes are dehydrochlorinated by alcohol alkali at 5–20°C. For TCB the reaction proceeds by the scheme:



The TCB yield is 58% under these conditions.

Certain patents^{4–7} describe vapor-phase and thermal methods of TCB synthesis by condensation of tetrachloroethylene with ethyl alcohol. The reaction proceeds for 1–60 s in the gaseous phase at 400–700°C, the unsaturated alcohol (1,1,2-trichlorobutene-1-3-ol) being isolated with 87% yield. The alcohol is dehydrated over activated aluminum oxide at 270–280°C in inert gas current, and TCB is obtained; its yield does not exceed 20%.

Patent⁸ describes a method of obtaining hexachlorobutane by interaction of monovinyl acetylene with chlorine in gaseous or liquid phase in the presence of solvents and catalysts. Later on, Armenian scientists improved this method and used it for TCB synthesis.

Babayan with co-workers⁹ mention a possibility of TCB synthesis with 70% yield by splitting a quaternary ammonium salt via the scheme:

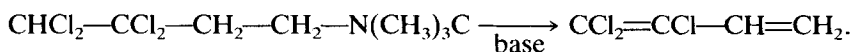
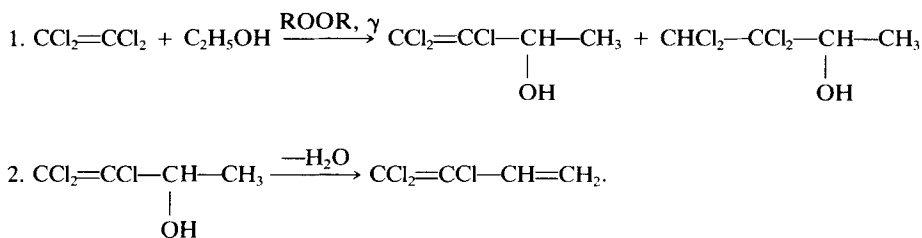


TABLE I
1,1,2-Trichlorobutadiene-1,3 properties

References	T _{boil} /°C/ mmHg	n _D ²⁰	d ₄ ²⁰
1,2	75 / 80	1,5355	1,3733
3	67 / 50	1,5340	1,3763
4 - 7	60 / 45	1,5327*	1,3710*
10	41 / 15	1,5290*	1,3740*

* at 25 °C

Matsuda and Imoto¹⁰ described a liquid-phase method of TCB synthesis by interaction of tetrachloroethylene with ethyl alcohol:



The initial components should be taken in the ratio 1:4; the reaction is carried out in the presence of organic peroxides or under γ -radiation in a nitrogen atmosphere at 83°C, followed by dehydration of the resulting 1,1,2-trichlorobutene-1,3-ol over phosphoric anhydride or aluminum oxide at 225°C. The TCB yield is 50%.

Table I presents the characteristics of TCB obtained by various methods.

2. SYNTHESIS, STRUCTURE AND PROPERTIES OF POLYMERS AND COPOLYMERS OF 1,1,2-TRICHLOROBUTADIENE-1,3

Kolesnikov *et al.*¹¹ were the first to describe TCB polymerization and to show, that the monomer is polymerized readily with 70–90% yield in the presence of radical initiators. In subsequent investigations these authors studied in detail TCB radical polymerization in mass, emulsion and solution^{12–14} and showed that the mass polymerization of TCB proceeds readily at heating, but the presence of radical initiators accelerates the process and makes it possible to decrease the reaction temperature (Table II).

In the emulsion polymerization of TCB the polymer yield is practically quanti-

TABLE II

Effect of initiator nature on TCB polymerization. The reaction conditions: In mass, 0.5 mol.% of initiator, 80°C, 4 h; In emulsion; monomer/water/emulgator initiator = 100/180/5/0.3 (by mass), 50°C, 10 h; In solution, 0.5 mol.% of initiator, solvent-toluene, the monomer concentration-mol./l, 80°C, 10 h.

Initiator	mass		emulsion		solution	
	yield, %	$[\eta]$, dl/g	yield, %	$[\eta]$, dl/g	yield, %	$[\eta]$, dl/g
Without initiator	21,5	0,33	-	-	-	-
Benzoyl peroxide	88,5	0,39	51,5	1,5	48,5	0,08
Axo-bis isobutyronitrile	75,5	0,30	99,8	3,3	46,5	0,09
Tert-butyl peroxide	28,5	0,19	-	-	-	-
Cumene hydroperoxide	29,5	0,30	-	-	29,5	0,12
Tri-n-propylboron	24,0	0,17	-	-	-	-
Potassium persulfate	-	-	96,0	3,4	-	-
Ammonium persulfate	-	-	96,5	3,2	-	-

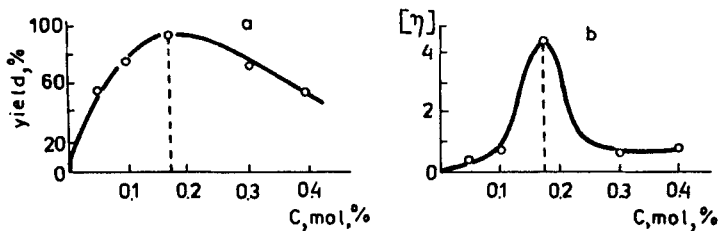


FIGURE 1 Dependencies of the polymer yield (a) and intrinsic viscosity (b) on initiator concentration in TCB emulsion polymerization.

tative and molecular mass is as much as several millions. When TCB is polymerized in solution only the low-molecular polymers are produced; their yield is about 50%.

The investigation of the effect of reaction conditions on the yield and intrinsic viscosity ($[\eta]$) of PTCB shows that when an initiator concentration in the TCB mass polymerization is increased from 0.1 to 0.75 mol.% the polymer yield increases from 45 to 97% and the $[\eta]$ value from 0.23 to 0.39 dl/g.

Figure 1 shows dependencies of the polymer yield and intrinsic viscosity on the initiator concentration in the TCB emulsion polymerization. The maximal values of yield and intrinsic viscosity $[\eta]$ are attained at 0.17 mol.% $K_2S_2O_8$ content.

As is seen from Table III, the yield and the viscosity of PTCB, obtained in emulsion, are influenced markedly by the water:oil phase ratio in the initial mixture.

TABLE III

The influence of water:oil phase ratio on the emulsion polymerization of TCB

Water:oil	Yield %	$[\eta]$, dl/g
1,0 : 1	95,5	4,9
1,8 : 1	96,0	3,4
2,5 : 1	93,0	3,2
3,0 : 1	89,0	2,0

TABLE IV

The influence of the monomer concentration on the TCB polymerization in solution

Monomer concentration, mole/l	Yield %	$[\eta]$, dl/g
1	43,0	0,07
2	44,0	0,07
3	48,5	0,07
4	70,5	0,08
5	72,5	0,09
6	75,4	0,10

When TCB is polymerized in solution, an increase in the monomer concentration results in the increasing polymer yield (Table IV); however, when the concentration exceeds 6 mol./l reaction solutions become too viscous. Variations in solvent nature and initiator concentration from 0.5 to 2.0 mol. % influence little the yield and $[\eta]$ value of the polymer, obtained by the monomer polymerization in solution.

In all the polymerization methods, the temperature rise from 20 to 100°C increases the polymer yield, but decreases simultaneously the intrinsic viscosity, that is caused most probably by increasing the branching of macromolecules.

In studies on the reaction duration effect it was found that the polymer-limiting yield and maximum $[\eta]$ value are attained generally upon 4–5 h polymerization. Only in the mass polymerization the $[\eta]$ value continues to increase even when the polymer yield becomes constant; this appears to be caused by a gel effect.

The following optimal conditions of the TCB radical polymerization have been adopted on the basis of investigations¹²⁻¹⁴:

Mass polymerization: initiator—benzoyl peroxide (0.5 mol.%), 80°C, 6 h; the polymer yield is 99.9%; $[\eta] = 0.43$ dl/g (benzene, 25°C); $\bar{M}_n = 71\ 000$.

Emulsion polymerization: water/oil ratio = 1.8:1 initiator— $K_2S_2O_8$ (0.17 mol.% referring to monomer), emulsifier—5 mass% (referring to monomer), 50°C, 10 h; the polymer yield under these conditions is 95%, $[\eta] = 4.5$ dl/g, $\bar{M}_n = 3\,400\,000$.
Polymerization in solution: initiator—benzoyl peroxide (1 mol.%), solvent—toluene, monomer concentration 4 mol./l, 80°C, 10 h; the polymer yield is 69%, $[\eta] = 0.06$ dl/g, $\bar{M}_n = 3000$. Polymer composition: Found (calculated), %: C 30.55; 30.53 (30.51); H 1.83; 2.01 (1.92); Cl 67.05; 67.21 (67.57).

Kinetics of the radical polymerization of TCB, as well as of other chloro-derivatives of 2-chlorobutadiene, were studied by gas-liquid chromatography.¹⁵ The polymerization was carried out in benzene at 60°C, the monomer concentration was 7.58 mol./l, the initiator (benzoyl peroxide) concentration was 0.037 mol./l. Table V shows, that the TCB polymerization rate is comparable with the rate of 2-chlorobutadiene polymerization; the activation energy is of the same order of magnitude.

Paper¹⁶ describes the kinetics of radiation polymerization of TCB in solid and liquid phases (−196 to 55°C). The reaction rate is found to be proportional to radiation dose; diphenylpicrylhydrazyl is an inhibitor of the reaction. In the solid phase the polymerization rate is higher than in the liquid one; the activation energy values are 1.8 and 33 kJ/mol, respectively.

High pressure accelerates significantly the TCB polymerization: the PTCB yield ranges up to 95% and the $[\eta]$ value to 0.6 dl/g as soon as 1 h after the beginning of polymerization at 6000 atm. in the presence of azo-bis-isobutyronitrile (0.001 mass.%) at 40°C.¹⁷

Thus, TCB polymerization is found to proceed by a radical mechanism with high degree of conversion (99–100%). High-molecular and entirely soluble polymers are produced; gelation is not observed under the investigation conditions.

PTCB is white, fibrous or powdery (dependent on molecular mass) polymer, self-extinguishing, resistant to cold mineral-acid action, with a limited swelling ability in benzene and high adhesivity to metals and rubber. According to the X-ray structural analysis data, PTCB is an amorphous polymer, containing inhomogeneities, that give intense background on the X-ray diffractogram, typical for rubbers. The PTCB density is 1.44 g/cm³.

PTCB readily dissolves in cold aromatic and chlorinated hydrocarbons, dioxane, decaline and tetrahydrofuran. PTCB forms elastic films from solutions; their tensile

TABLE V

The polymerization rates (w) of 1,1,2-trichlorobutadiene and 2-chlorobutadiene

Monomer	$W \times 10^5$ mole/l.s	$K \times 10^5$, l/(moles)	K_p/K_0 0.5×10^2	E, (kJ/mole)	$A \times 10^{12}$ (cm ³ /s)
CH ₂ =CH-CCl=CH ₂	9,35	6,39	1,44	92,4	5,6
CH ₂ =CH-CCl=CCl ₂	4,13	2,83	0,64	94,6	4,4

TABLE VI

Mechanical properties of films obtained from PTCB of different molecular mass

$\bar{M}_n \times 10^{-3}$	δ , MPa	ϵ , %
25	Brittle film	Brittle film
100	5,7	730
630	8,8	830
1340	15,5	1000

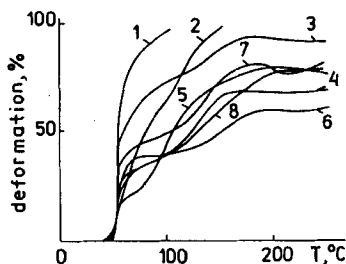


FIGURE 2 Thermomechanical properties of PTCB (10-g load at the 4 mm-diameter punch; rate of temperature increasing = 80°C per hour). M_{PTCB} : 25 000 (1), 80 000 (2), 100 000 (3), 200 000 (4), 380 000 (5), 470 000 (6), 630 000 (7), 1 340 000 (8).

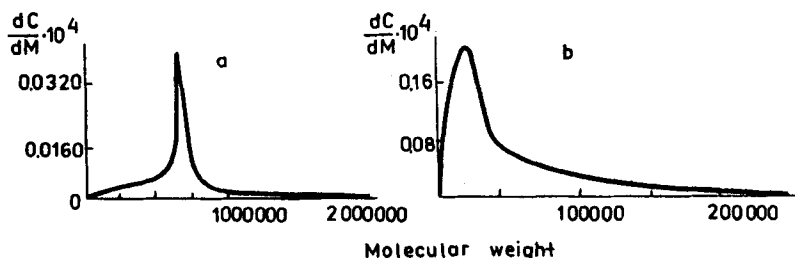


FIGURE 3 Differential curves of the molecular-mass distribution: emulsion PTCB (a), bulk-PTCB (b).

strength (σ) and breaking elongation (ϵ) increase with the increasing polymer molecular mass (Table VI).

Thermomechanical investigations showed that the PTCB glass transition point (T_g) is independent of molecular mass and is 55°C (Figure 2).^{11,18} A high-elastic state is observed in a limited temperature range for PTCB specimens with molecular mass above 80 000. The results of these investigations made it possible to estimate PTCB macromolecule flexibility and to determine the mechanical segment value, found to be about 25 000.

An examination of the thermomechanical curves, presented in Figure 2, shows,

that a viscous-flow state is absent for PTCB, because its flow temperature is higher than the temperature of chemical decomposition.

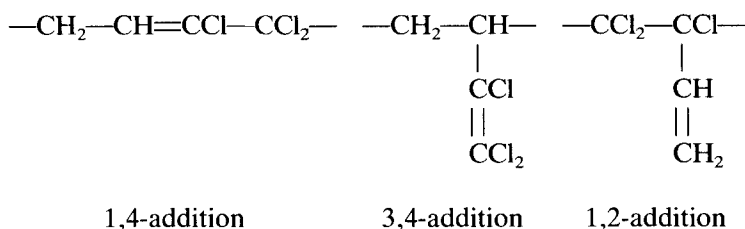
Pol'sman with co-workers¹⁹ studied chemical reactions of PTCB over a wide temperature range. Soboleva *et al.*^{20,21} investigated molecular-mass characteristics. They determined the following viscosimetric constants in the Mark-Kuhn-Houwink equation for the fractionated PTCB in benzene²⁰:

$$[\eta] = 3.16 \times 10^{-4} M^{0.66}$$

The increasing polymer polydispersity influences notably the $[\eta]$ dependence on M .

Investigation of the molecular-mass distribution for PTCB, obtained by the mass and the emulsion polymerization under optimal conditions,²¹ showed that even at a high degree of conversion the emulsion polymer shows a narrow distribution in the main part and a long high-molecular "tail" (Figure 3). The polydispersity parameter for this polymer calculated from the distribution curve, $\bar{M}_w/\bar{M}_n = 1.55$. The distribution for the bulk PTCB is broader ($\bar{M}_w/\bar{M}_n = 2.04$).

In the course of the TCB polymerization the three types of additions of the monomer units may be expected:



According to quantum chemical calculations, presented in Reference 15, the first and fourth carbon atoms in the molecules of chloro-derivatives of 2-chlorobutadiene are most reactive: the highest values of free-valence indexes correspond to them. The monomer π -electron system is polarized in such a way that under the radical-polymerization conditions an initiator attacks the fourth carbon atom. The presence of two chlorine atoms at the first carbon atom in 1,1,2-trichlorobutadiene-1,3 stabilizes a growing radical. The chlorine atoms do not create notable steric hindrances for polymerization, therefore the predominant 1,4-addition should be expected in the TCB polymerization.

Some of the authors investigated the structure of PTCB, obtained by the radical polymerization, using both physicochemical and spectral methods. Pavlova *et al.*²¹ found the 1,4-addition units in studies of PTCB properties in solutions. Nesmeyanov *et al.*¹ showed the presence of the 3,4-addition units in the polymer treated by anhydrous nitric acid.

Information on quantitative ratios of various units in the PTCB structure is obtained by spectral methods. Two absorption bands, 1600 and 1650 cm^{-1} , are observed in the region of double-bond frequencies in the IR spectrum of PTCB, 1650 cm^{-1} band markedly prevailing. According to the IR spectra of model low-

molecular compounds, the 1650 cm^{-1} band was ascribed to the double-bond vibrations in the 1,4-addition units, and the 1600 cm^{-1} band, to those ones in the 3,4-addition units.^{16,22}

The locations of CH— frequencies in the PTCB IR spectrum do not contradict this conclusion; the four absorption bands are observed in the region of C—H vibrations: 2865 , 2935 , 2970 and 3080 cm^{-1} . The bands 2865 , 2935 and 2970 cm^{-1} are characteristic of vibrations of —CH₂— group, that may be present in the 1,4- and 3,4-addition units. The 3080 cm^{-1} band is characteristic of —CH= group vibrations.

Presently, the PTCB structure has been investigated in detail by ¹H and ¹³C NMR spectroscopy. PTCB is found to contain the two structures, produced by the addition of units in the 1,4- and 3,4-positions in the ratio 85:15 mol.% (within 5% error).

The authors of paper²³ obtained the ¹H-NMR spectra of 10% PTCB solutions in CDCl₃ with "Bruker WP-200-SJ" spectrometer operating at 200.13 MHz; HMDS ($\delta = 0.05\text{ ppm}$) was used as an internal reference. ¹³C-NMR spectra were registered with "Bruker WP-SI" operating at 50.31 MHz frequency under the conditions providing an absence of the Overhäuser effect. The "IMODECHO" regime was used, where nuclei of the carbon atoms, associated directly with the even and odd numbers of hydrogen atoms, appear as the signals of different polarity.

In the ¹H-PTCB spectra methylene and olefinic protons of the 1,4-addition units of "head-to-tail" type give partially overlapped doublet and triplet signals in the regions 3.45–3.50 and 6.43–6.75 ppm, respectively (³I_{HH} = 5.7 Hz), the ratio of integral intensities being equal to 2. Protons of methylene and methin groups of 3,4-addition units show two slightly resolved multiple signals, centered at 1.78 and 3.00 ppm, respectively. There is observed also a multiplet, centered at 2.56 ppm, assigned to methylene protons of the 1,4-structures arising due to an anomalous addition of "head-to-head" type.

In the ¹H spectrum of copolymer of TCB with phosphorus-containing monomer two signals were observed in the region, characteristic of the olefinic protons of PTCB 1,4-units, 6.61 and 6.44 ppm, which were attributed to *trans*- (72%) and *cis*- (28%) proton positions relative to chlorine atom.²⁴

Table VII presents the chemical shifts in the ¹³C-NMR spectra, detected in studies of the PTCB structure by this method. The signals of 1,4-addition units are most intensive. The ratio between 1,4- and 3,4-structures in PTCB is found to be in-

TABLE VII

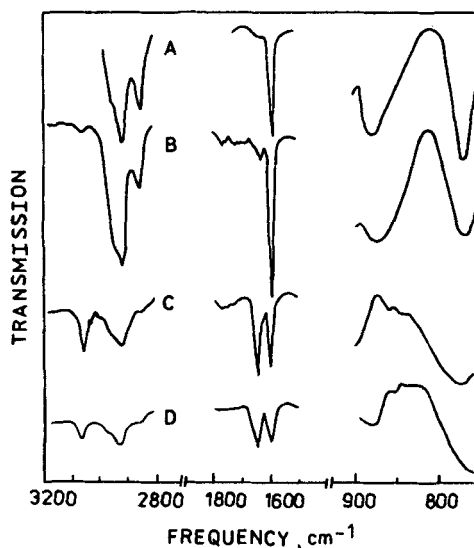
Chemical shifts in the ¹³C-NMR spectrum of poly 1,1,2-trichlorobutadiene-1,3

1,4-addition				3,4-addition			
—CCl ₂ —	=CCl—	=CH—	—CH ₂ —	=CCl ₂	=CCl—	—CH ₂ —	—CH—
87,45	136,17	124,54	46,31	119,62	133,34	31,36	38,58
88,23	136,82	126,84	46,34	121,24	133,70	33,33	40,26

TABLE VIII

The emulsion polymerization of TCB in the presence of the redox initiating systems

Initiating system	Yield	$[\eta]$, dl/g	$\bar{M}_n \times 10^{-3}$	Content Cl, %
Tert-butyl peroxide +Fe ₂ SO ₄	90	0,72	120	66, 19; 66, 35
Benzoyl peroxide +Fe ₂ SO ₄	85	0,64	100	-
Cumene hydroperoxide + rongalite	27	0,76	130	66, 18; 66, 05
Ascorbic acid +Fe ₂ SO ₄	89	0,66	100	-

FIGURE 4 IR spectra of 1,1,2-trichlorobutadiene-1,3 at -196°C (A), -78°C (B), 0°C (C), $+55^{\circ}\text{C}$ (D).

dependent of increasing chain length: the ^{13}C spectra of PTCB are identical for polymers with $M = 7000$ and $M = 200\,000$.

Some of the authors investigated possibilities of controlling PTCB chain structure in order to modify its properties. Attempts at stereospecific polymerization of TCB (and other halogenodienes) with the use of complex metal-organic catalysts of $\text{CoCl}_2\text{AlCl}_3$ type have not been successful: a coloured, low-molecular polymer with low chlorine content was produced.²⁵ Only the polymer traces were isolated upon TCB polymerization in the presence of catalysts for cation polymerization (boron trifluoride, titanium tetrachloride).¹¹

High-molecular soluble polymers with high adhesivity to rubber and metals were obtained on radical emulsion polymerization of TCB in the presence of redox systems, which allowed a lowering of the reaction temperature to $2\text{--}4^{\circ}\text{C}$ (Table

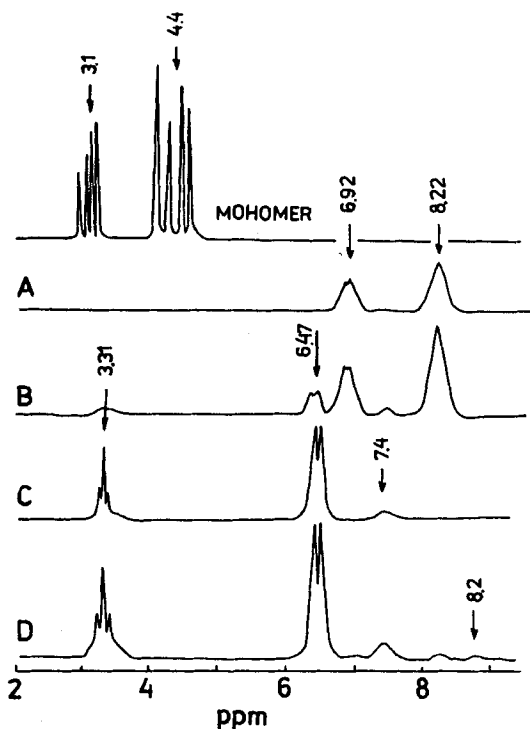


FIGURE 5 PMR spectra of 1,1,2-trichlorobutadiene-1,3 and its polymers obtained at -196°C (A), -78°C (B), 0°C (C), $+55^{\circ}\text{C}$ (D).

VIII).⁸ On evidence derived from $^1\text{H-NMR}$ the polymers synthesized under these conditions contain ca. 30% of 3,4-structures. Such a variation of the polymer structure resulted in T_g increasing from 55 to 85°C , that markedly enlarged the temperature operation range.²⁶

Makarova *et al.*^{27,28} obtained PTCB containing ca. 40% of the 3,4-structures upon the TCB polymerization under the combined action of shear deformation and high pressure on Bridgman anvil at 153–250 K. The authors explain changes in polymer structure by dramatic disintegration of the monomer crystal lattice due to plastic deformation under the experimental conditions.

Matsuda and Fujii¹⁶ studied TCB polymerization initiated by γ -radiation of ^{60}Co in the range from -196 to $+55^{\circ}\text{C}$ and showed that the liquid-phase polymerization of this monomer at low temperatures ($T_m = -48.5^{\circ}\text{C}$) proceeds by a radical mechanism and produces predominantly the 1,4-structures. At lower temperatures in solid phase the polymerization proceeds by an ionic mechanism to give predominantly the 3,4-addition units. Figures 4 and 5 present the IR and PMR spectra of PTCB specimens, synthesized at various temperatures by γ -radiation polymerization.

PTCB enriched by the 3,4-structures appears to have an increased thermal stability: on heating to 210°C the bands in the IR spectrum corresponding to the 1,4-structure disappear completely, whereas 1600 and 780 cm^{-1} bands corresponding to the 3,4-structure are retained.¹⁹

TABLE IX

The copolymers of TBC with different unsaturated compounds

Comonomer	TBC content in polymer mole. %	Solubility	Tg, °C	Beginning of thermal degradation, °C	References
Styrene	30 - 85	Soluble	55-75	150	29-31
Acrylic and methacrylic acids	53 - 98	Soluble when TBC > 75 mole. %	80-90	150-200	32-34
Esters of α -cyanoacrylic acid	30-80	Soluble when TBC > 75 mole. %	80-100	250-350	35-39
Esters of 2-methyl-1,3-butadiene thionphosphonic and phosphonic acids	20-81	Soluble	-	220-250	24
No3 and No4 (Triple copolymer)	80-95	Soluble	-	-	39
Acrylonitrile	31-86	Soluble when TBC > 60 mole. %	40-55	-	29
No2 and No6 (Triple copolymer)	74	Soluble	-	-	34
Vinylchloride	61-86	Soluble	50	-	29
Bicyclo (2,2,1) - heptadiene 2,5	36-88	Soluble	130-140	-	29
Vinylacetate	>50	Soluble	0	-	18
Trichloroprene, trifluorostyrene methyl methacrylate	>50	Soluble	-	-	40 18
Methyl, ethyl, vinyl ketones	>50	Soluble	-	-	40

TABLE X

The constants of copolymerization of TBC with styrene

Reaction Conditions	C_1 (TCB)	C_2 (styrene)	References
In mass, benzoyl peroxide 60°C	$1,18 \pm 0,08$	$0,07 \pm 0,03$	29
In benzene, benzoyl peroxide 70°C	$1,10 \pm 0,05$	$0,12 \pm 0,04$	15
In mass, γ -radiation 25° and -78÷196°C	1,75	0,15	30

Numerous investigations showed that TCB is not only readily polymerized by a radical mechanism but it is also readily copolymerized with various unsaturated compounds (Table IX). The copolymerization of TCB with different monomers was studied in mass, emulsion and solution; it was found, that the most high-molecular copolymers are usually produced in emulsion copolymerization.

In studies of TCB reactivity in the radical copolymerization, styrene was taken as a reference monomer.^{15,29,30} Table X presents TCB copolymerization constants with styrene found by different authors; the values show that TCB is a more active monomer in the copolymerization reaction than styrene. The following values of Alfrey and Price parameters have been found for TCB: $Q_1 = 2.66$, $e_1 = 0.63$ (for styrene they are: $Q_2 = 1$, $e_2 = -0.8$).¹⁵ The value of activity factor Q_1 is high; however, it is less than for chloroprene.^{7,26}

Table IX shows that TCB copolymers with various unsaturated compounds are enriched, as a rule, by TCB units in comparison with the starting mixture of monomers; they are soluble in various organic solvents (except the copolymers containing 25 mol.% of an acrylic component). The copolymers form films and coatings from solutions which have a higher strength but lower elasticity in comparison with homo-PTCB. For example, for the copolymers of TCB with esters of α -cyanoacrylic acid the following values are found: $\sigma = 37\text{--}49$ MPa, $\epsilon = 3\text{--}7\%$ (for homo-PTCB synthesized under the same conditions $\sigma = 2$ MPa, $\epsilon = 1000\%$ ³⁶).

The value of the glass transition point of PTCB can be varied by introduction of foreign units in the chain; the polymer properties change from rubber-like (copolymers with vinylacetate) to plastic (copolymers with acrylic monomers, bicyclo-[2,2,1-heptadiene-2,5]).

Copolymerization of TCB with acrylic acids, esters of α -cyanoacrylic acid, 2-methyl-1,3-butadiene thionphosphonic acid increases markedly the polymer stability in thermooxidative degradation. TCB copolymers with acrylic acid form more elastic films than does PTCB ($\epsilon = 1500\text{--}1700\%$, $\sigma = 1.2\text{--}1.4$ MPa).

It should be noted that all copolymers containing more than 20 mol.% of TCB retain inherent high adhesivity and flame resistance. Simultaneous presence of chlorine and phosphorus in the copolymers (specimen no. 4 in Table IX) decreases their flammabilities; the values of the oxygen index for the copolymers are 21–45.²⁴

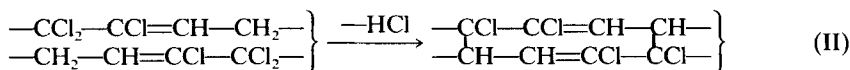
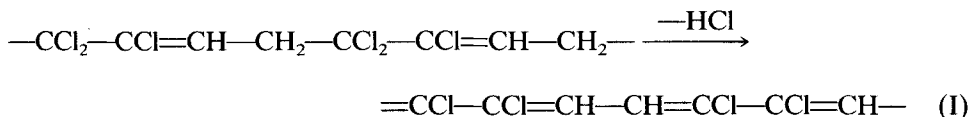
In studies of TCB copolymers with the ethyl ester of α -cyanoacrylic acid²³ and the dimethyl ester of 2-methyl-1,3-butadiene thionphosphonic acid²⁴ it was established by IR and NMR spectroscopic methods, that the 1,4-addition of "head-to-tail" type is the predominant structure in the copolymer obtained by radical copolymerization as well as in the homopolymer; the anomalous "head-to-head" addition units and the 3,4-addition units are present in minor amounts.

3. CHEMICAL REACTIONS OF POLY(1,1,2-TRICHLOROBUTADIENE-1,3)

The presence of 80–90% of normal linear-addition units (1,4-units) in the structure of PTCB is the cause of the high reactivity of this polymer in reactions both with low-molecular reagents (polymer-analogous reactions) and with high-molecular

compounds (interpolymer reactions). In the course of these reactions, allyl-chlorine or hydrogen atoms are replaced; addition to a double bond is also possible. In the substitution reactions of PTCB an allyl rearrangement (well-known for low-molecular compounds) is usually observed.⁴¹

Due to the high mobility of allyl atoms of chlorine and hydrogen, a thermal treatment of PTCB leads usually to its partial dehydrochlorination, that can proceed by intra- (Scheme I) or intermolecular way (Scheme II). Polyene structures or interchain crosslinks are formed in these processes, respectively:



The authors of paper¹⁹ studied chemical reactions of PTCB over the temperature range from 120 to 340°C by mass spectrometry, differential thermal analysis and IR spectroscopy. The differential thermal analysis showed that from 140°C and on in PTCB the processes proceed followed by mass loss, that is principally a result

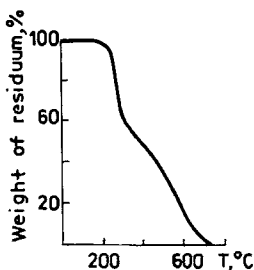


FIGURE 6 Dynamic thermogravimetric analysis of PTCB in air.

TABLE XI

Structure of PTCB under action of AlCl_3 (in nitrobenzene, PTCB concentration is 5 g/dl, 20°)

Time (min)	Gel yield, %	Cl, %	Conversion of allyl chlorine, %	d, g/cm ³	K	m_{sw}/m_d^*
20	27	65,69	15,9	1,428	0,600	8,2
40	68	65,34	19,8	1,422	0,599	6,3
60	77	60,97	68,7	1,345	0,605	5,4
120	88	59,84	81,7	1,312	0,578	4,4

* The ratio of swollen polymer mass to dry mass (chloroform, 25°C)

of the hydrogen chloride elimination, on evidence derived from the mass-spectrometric data (Figure 6).

On differential thermal analysis (DTA) and differential thermal gravimetric (DTG) curves there are two distinct maxima indicating that HCl evolution occurs in two steps. The first dehydrochlorination step in the range 150–210°C is related to the intramolecular splitting out of HCl. This process is followed by disappearance in the IR spectrum of the 1650 cm^{-1} band, corresponding to vibrations of the double bonds in linear-structure PTCB, and by an increase in intensity of the 1625 cm^{-1} band, characteristic of the polyene structure. In the IR spectrum of heated PTCB the 710, 760, 870, 1235, 1270 and 1335 cm^{-1} bands also disappear.

The second dehydrochlorination step begins at 240°C and appears to be connected with splitting out of the less mobile chlorine atom located at a double bond. This process manifests itself in the broad absorbance in the 1530–1670 cm^{-1} region, which is most likely a result of overlapping of valent vibration bands characteristic of the conjugated double bonds in polycyclic and polyene fragments of macromolecules.

UV radiation induces the interchain crosslinking processes in PTCB.⁴² Upon 20 h radiation at 0°C the density of the polymer network reaches the limiting value, following which the degradation processes in the polymer predominate. Latexes of PTCB were found to be most resistant to radiation; the polymers dissolved in benzene produced crosslinks most readily.

Interchain crosslinking of PTCB under the action of AlCl_3 was studied in Reference 43; the gel yield was shown to increase and the chlorine content in the polymer to decrease in the course of time (Table XI).

Contributions of intra- and intermolecular processes of PTCB dehydrochlorination in overall conversion of allyl chlorine were calculated from the glass-transition points of the initial and the dehydrochlorinated polymers. The calculations showed that the interchain crosslinking is related with only 4.8% of the total conversion of allyl chlorine (81.7%); the other 76.9% of the conversion is connected with the intramolecular dehydrochlorination of PTCB.

It is seen from Table XI, as the dehydrochlorination reaction of PTCB proceeds, the density (d), the molecular packing coefficient (K) and the degree of swelling (m_{sw}/m_d) decrease.

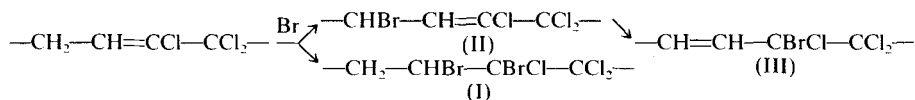
Thus the interchain dehydrochlorination of PTCB leading to crosslinking occurs only under rigid conditions in the presence of dehydrochlorinating agents, in contrast to the intramolecular process.

Evsyukov⁴⁴ has found that the dehydrochlorinating system, consisting of a saturated KOH solution in ethanol and tetrahydrofuran, results in the entire loss of solubility and the black colour of the PTCB film upon a 20-min contact at 20°C. The absorption bands in IR spectra characteristic of the initial PTCB disappear completely after such treatment of the film. The electron Auger spectroscopic method showed the presence of polyine (d -carbide) as well as polyene structures in the reaction products.

PTCB readily enters into various polymer-analogous reactions (bromination, arylation according to Friedel–Crafts, amination), as well as the interpolymer Friedel–Crafts and Hoffmann reactions, proceeding by multiple chemical inter-

actions of PTCB with a second macroagent, that contains reactive functional groups in repeating units of the reacting macromolecules.

Bromination of PTCB was carried out with a free bromine or bromosuccinamide in boiling CCl_4 in the presence of benzoyl peroxide; bromine (20–25%) was introduced into the PTCB structure under these conditions. An analysis of the IR spectra of bromo-PTCB showed that the two reactions proceed under PTCB treatment with bromine: the bromine addition to double bonds (Scheme I) and the bromine substitution for the allyl hydrogen (Scheme II):



Simultaneously the cyclization occurs under the synthesis conditions at the joints of the 3,4-addition units with the brominated 1,4-units: it proceeds in several stages involving dechlorination, dehydrobromination and allyl rearrangement.

The main reaction in PTCB interaction with bromosuccinamide is the substitution of bromine for the allyl hydrogen (Scheme II), followed by the allyl rearrangement with bromine migration (Scheme III).

The PTCB bromination proceeding only at high temperature is followed by the polymer degradation and also by its crosslinking at the deeper stages of the reaction.

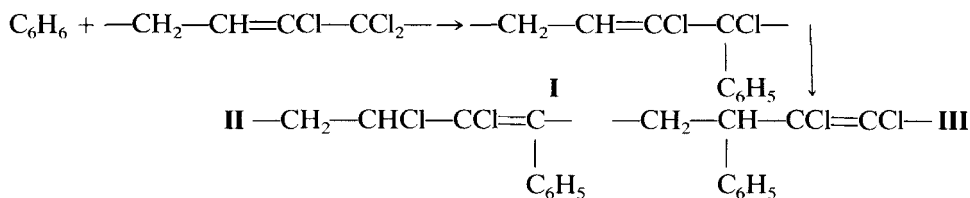
Polymers with more homogeneous structure containing ca. 20% of bromine were obtained by bromination in the presence of SnCl_4 at room temperature; the reaction is supposed to proceed by an ionic mechanism.

Br-PTCB is a slightly coloured, powdery polymer, highly soluble in aromatic and chlorinated hydrocarbons. On bromination by free bromine the polymer retains a capacity for film forming, the film strength increasing from 5 to 18 MPa and relative deformation decreasing from 500 to 5%.

An increase in the bromine content in the polymer enhances T_g values and improves adhesivity and flame resistance: thermal degradation of Br-PTCB with notable mass loss begins at 140–150°C, as in the case of the initial PTCB. Heated at 120°C, for 1 h Br-PTCB retains solubility, whereas PTCB ceases to dissolve.

Vointseva *et al.*^{46–49} showed that PTCB reacts with benzene, toluene, ethylbenzene and tetraphenyl lead in the presence of Friedel–Crafts catalysts (AlCl_3 , AlBr_3 , FeCl_3 , SnCl_4). The reactions proceed at 5–40°C in an aromatic solvent, which acts simultaneously as a reagent, or in nitrobenzene. As a result of such interaction, an aromatic radical enters the chain. Thus, PTCB becomes significantly modified but retains inherent self-extinguishing and adhesive properties.

It is found by the example of the interaction between PTCB and benzene that in the course of this reaction an allyl chlorine is replaced by phenyl (Structure I), followed by the allyl rearrangement in the polymer chain, which leads to a migration both of chlorine (Structure II) and of phenyl (Structure III):



A calculation of $^1\text{H-NMR}$ spectrum showed that the obtained polymer contains 70% II, 19% III, and 11% 3,4-addition units of the initial polymer (the calculation accuracy is within 1%).

A variation of the reaction conditions produces the polymers with different degrees of the substitution of C_6H_5 for Cl until it becomes practically complete (~90%).

From the amount of HCl evolved in the reaction, as well as the results of spectroscopic studies and elemental analysis, it was established that only one of the allyl chlorine atoms is replaced by phenyl in the course of the reaction. This appears to be connected within the migration of the second chlorine atom during allyl rearrangement.

The arylated PTCB retains a solubility in all organic solvents typical for PTCB; when the degree of substitution is below 80% the polymer intrinsic viscosity is higher than that one of the initial polymer. Table XII shows that as the substitution degree of C_6H_5 for Cl increases, the T_g value and the strength of the polymer films increase, but the relative deformation decreases. The polymer thermal resistance increases simultaneously: the completely substituted polymer loses only 5% of the initial mass at heating in air to 300°C .

A modification of PTCB with amines is proved to be very interesting and promising for practical purposes.⁵⁰⁻⁶¹ Amines react with PTCB as dehydrochlorinating agents: the chlorine content in the polymer modified by amines is reduced from the initial 67 to 40-50%; the reaction is accompanied by the black colouring and

TABLE XII
Properties of PTCB modified with benzene

Degree of Substitution -C on $-\text{C}_6\text{H}_5$, %	T_g , $^\circ\text{C}$ x)	σ , (MPa)	ϵ , %
0	0	2,5	1040
8	30	6,0	500
28	40	8,0	400
46	80	10,5	30
78	105	24,0	20
90	120	brittle film	

x) T_g was determined with films under 50 kg/cm² loading

the loss of solubility. At the same time, the amine moiety enters the polymer chain, as indicated spectroscopy. The reaction products contain ca. 3% nitrogen, thus substitution of the amine group for the chlorine atom occurs, along with the dehydrochlorination.⁵⁰

The activation energy of the thermal dehydrochlorination of PTCB determined from the rate measurements of HCl evolution,⁵¹ was found to be 159 kJ/mol and to decrease to 125 kJ/mol in the presence of pyridine and the methylvinylpyridine rubber (SKMVP).

An absorption band in the region of 450–550 nm was revealed in the electron-absorption spectra of the products of PTCB interaction with various amines (mono-, di-, and triethylamine, diethylaniline, pyridine, SKMVP). This band denotes that the reaction proceeds through formation of a charge-transfer complex (CCT); this is quite natural for the system containing a donor (amine) and an acceptor (PTCB).

The CCT formation in the course of the interaction of PTCB with the amines is evidenced also by a rise of the narrow ESR singlet with a *g*-factor close to that of a free electron.^{52,53}

According to work,⁵¹ secondary reactions of CCT are of the free-radical nature, and therefore pyridine rubber and SKMVP accelerate markedly the crosslinking between PTCB and polyisoprene (similar processes occur in the course of vulcanization, when an adhesion bond is produced between rubber and other substrates by use of adhesive compositions based on chlorine-containing polymers).

The NQR method showed that the amines react with allyl chlorine atoms of PTCB: two signals at 35.8 and 37.3 MHz are observed in the NQR spectra, attributed to =CCl— and —CCl₂— groups, respectively. In PTCB modified by diethylamine (DEA) the signal from —CCl₂— group vanishes, whereas the signal at 35.8 MHz is retained.⁵⁰

The IR spectrum of PTCB contains two absorption bands in the region of $\nu_{\text{C—Cl}}$ valent vibrations, assigned as follows: 765 cm⁻¹ to C—Cl at a double bond and 720 cm⁻¹, to allyl $\nu_{\text{C—Cl}}$. As the reaction of PTCB with the amines proceeds, the ratio of optical densities D_{720}/D_{765} decreases, i.e. the reaction occurs due to the allyl chlorine atoms.⁵⁴

PTCB reacts not only with low-molecular amines but also with high-molecular polymers containing an amine group in repeating units of the polymer chain, for example with poly(ethylene imine) (PEI).^{52–56} In the IR spectrum of the interpolymer the valent vibrations' band of the PTCB allyl chlorine and of the PEI NH group (3200–3500 cm⁻¹) decrease, and there appears the band at 1260 cm⁻¹, characteristic of the valent vibrations of the tertiary amine C—N bond.

Figure 7 shows, that in the electron-absorption spectra of the products of PTCB interaction with PEI, besides the band of the charge transfer (450–550 nm), there is an additional band at 300 nm typical for conjugated structures; it arises in the modified polymer as a result of the dehydrochlorination of PTCB under the amine action.

By taking into account the macromolecular nature of the reagents it was assumed that only a fraction of units of each of the polymers participates in the reaction. However, the degree of conversion in the interaction of PTCB with PEI was shown⁵³

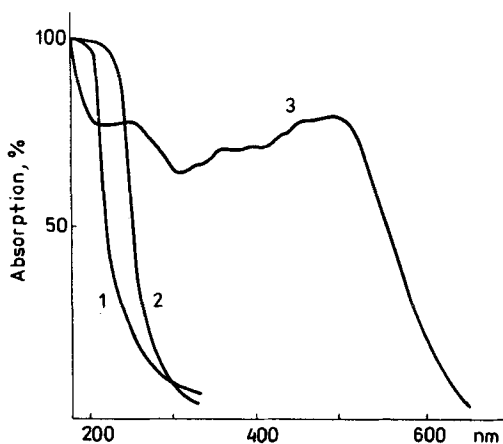


FIGURE 7 Electron absorption spectra of polymers: PTCB (1), PEI (2), interpolymer PTCB:PEI = 33:67 mol.%.

to range up to 80–85%, the reaction rate and degree being higher than those in the PTCB interaction with DEA.

The authors relate the great depth of the interpolymer reaction to uncoiling of macromolecular chains as the reaction proceeds (the polyelectrolytic effect). An increase in the rate of the reaction between PTCB and PEI is accounted for the formation of the interpolymer donor–acceptor complex in the course of the reaction (cooperative effect).

The interaction of PTCB with PEI produces crosslinked products or entirely soluble interpolymers, dependent on the reaction conditions. Brilliant, durable films and coatings can be prepared from solutions of the interpolymers. Paper⁵⁴ describes the influence of the reaction conditions on the gelation process during the interaction between PTCB and PEI.

The reaction of PTCB with PEI proceeding through CCT formation is completed by formation of the covalent C—N bonds in some units of the polymer chain. Due to the macromolecular nature of the reagents and conformational effects of the polymer chain the resulting polymer contains structurally different units: (1) the interchain covalent bonds form the polymer network, in which the donor–acceptor complexes with the different charge-transfer rates (from weak diamagnetic ones up to ion-radical pairs) are incorporated; polyconjugated chain fragments, arising as a result of the intramolecular PTCB dehydrochlorination; (2) unreacted units of the initial polymers. Such a structure of the interpolymer predetermines the complex of its mechanical and conducting properties and opens the way for their regulation.

Due to the presence of polyconjugated fragments and strong paramagnetic CCT, the electrical conductance of the interpolymers is similar to that of the undoped polyacetylene (the specific volume resistance $\rho_v \approx 10^6 \Omega \cdot m$). The interchain covalent bonds impart strength to polymer films (breaking strength is about 40 MPa), which is comparable with that of such typical dielectrics as poly(vinyl chloride) and polyethylene (≈ 10 –40 MPa). Unreacted PTCB units impart the following properties to the interpolymers: a capability for deformation (relative deformation is

about 30%), the high adhesivity, the inherent property of PTCB, as well as an ability to be doped by introducing low-molecular tertiary amines in the interpolymer.

Papers⁵⁶⁻⁶⁰ consider electrophysical properties of PTCB with PEI reaction products in comparison with properties of the products of PTCB reaction with diethylamine.

It should be noted that the degree of crosslinking in the PTCB reaction with poly(ethyleneimine) is higher than in the reaction with diethylamine (in the latter case the degree of the polymer swelling is higher, as is seen from Table XIII). As a result, the interpolymer films have the higher mechanical strength (σ) and lower deformation (ϵ), than the products of the polymer-analogous interaction of PTCB with diethylamine; the specific electrical resistance of the interpolymer films is 3-4 orders of magnitude lower.

PTCB is found to react not only with amines but also with amides, for example, with dimethylformamide, polyamido-*m*-carboranes^{50,61} and with guanidine derivative, poly(hexamethylene guanidine) (PHMG).⁶²

Insoluble, yellow, elastic, self-extinguishing interpolymers were produced on interaction between PTCB and poly(*p,p'*-diphenylene-*m*-carborane amide). They appeared to be more stable to thermooxidative degradation than the initial polymers.

An interaction of PTCB with water-soluble poly(hexamethylene guanidine) was studied in an aqueous organic solvent system because of the absence of a common solvent for these polymers. In the course of the reaction an interaction occurs on the interface of the two polymers; a coloured reaction product (interpolymer) passes into organic phase, and then it can be readily processed into films and coatings. The interpolymer obtained retains the bactericidal properties inherent to PHMG, as well as the flame resistance inherent to PTCB and high adhesivity to various materials including Teflon. A coating from PTCB and PHMG interpolymer can be used for protection of surfaces in aqueous media⁶³ and for protection of swimming baths against biofouling and bactericidal contamination.

PTCB was used as a model compound in a series of studies⁶⁴⁻⁸⁶ devoted to general relations governing the interpolymer chemical reaction between two in-

TABLE XIII

Properties of the PTCB reaction products in the interpolymer reaction with PEI and in the polymer analogous reaction with diethylamin (DEA)

PTCB: amine (mole.%)	σ , (MPa)		ϵ , %		m_{sw}/m_d^*	
	PEI	DEA	PEI	DEA	PEI	DEA
75:25	18	2,5	170	1000	2,0	solution
33:67	37	6,6	50	530	1,4	23,0
25:75	23	9,6	36	340	1,2	15,3

(Footnote)* The ratio of swollen polymer mass to dry mass (chloroform, 25oC)

compatible polymers (by example of PTCB interaction with polystyrene [PS] under conditions of Friedel–Crafts reaction).

These works are generalized in reviews,^{75,86} and here we shall consider briefly the peculiarities of the structure and properties of the interpolymers produced in the interchain interaction between PTCB and PS. This reaction was carried out in the presence of AlCl_3 in common for the two polymer solvents (nitrobenzene, chlorinated hydrocarbons). Only soluble interpolymers were found to be formed when the concentration of the initial polymer mixture in solution was below the overlapping threshold of the macromolecular coils in this solvent; at higher concentrations a gel formed in the system sooner or later.⁸² In contrast to the polymer-analogous and crosslinking reactions of homo-PTCB, the yield of crosslinked polymer in the interpolymer reaction can attain 100%.

Whereas the reacting polymers are practically linked entirely to one another, the reaction depth (the conversion of functional groups) does not exceed 1–10%. It ranges up to 90% in the corresponding polymer-analogous reaction (the interaction of PTCB with benzene). This difference in the depths of the interpolymer and the polymer-analogous reactions is associated with difficulties in interpenetration of foreign macromolecular coils of the incompatible polymers; as a consequence, the majority of the functional groups located inside the coil are not accessible for reaction.

Various physicochemical methods showed that the molecules of interpolymers produced in solution are macromolecular coils swollen in the solvent; they consist of a few partially interpenetrated initial macromolecular coils that are associated by chemical bonds in an interpenetration zone. Such a structure of the interpolymers predetermines their physical and chemical properties.

It was found by the method of dynamic mechanical analysis that the interpolymers of PTCB and PS have two-phase structures.⁷⁸ However, electron microscopic in-

TABLE XIV

Mechanical properties of films obtained from the interpolymers and the mixtures of PTCB and PS homopolymers

Content PTCB, mole %	Interpolymer			Mixture of Polymers		
	σ (MPa)	ϵ , %	$E \times 10^{-3}$ (MPa)	σ (MPa)	ϵ , %	$E \times 10^{-3}$ (MPa)
100	-	-	-	2,5	1100	0,37
75	11,0	8	0,76	2,4	139	0,18
50	29,0	4	1,72	10,8	7	0,96
34	32,0	4	1,79	25,0	4	1,64
10	36,0	5	1,68	30,0	2	2,01
0	-	-	-	32,0	5	1,89

TABLE XV
Properties of PTCB, PS and their interpolymers

Polymer	Flame Resistance			Adhesion
	Burning, Smoldering, Mass loss,			Strength, (N/m)
	(s)	(s)	(%)	(to steel)
PTCB	no	2.2	5	350
PS	135	no	100	no
Interpolymer				
50:50 mol.%	no	1.4	18	260

vestigations show that, in contrast to the homogeneous structure of the statistical copolymers and the rough two-phase structures of mechanical mixtures of the homopolymers, the rare chemical bonds between the macromolecules of the interpolymers provide formation of the fine heterostructure regulated both by the ratio of components and by the concentration of crosslinks.⁸³

The interpolymers based on PTCB and PS are mechanically uniform and optically transparent, in contrast to the mechanical mixtures of the homopolymers, which are characterized by a distinct phase segregation on the macrolevel. Table XIV shows that the values of breaking stress (σ) and elastic modulus (E) for the interpolymers are higher than the corresponding values for the mechanical mixtures of the polymers practically over all the range of compositions.

The interpolymers of PTCB and PS retain individual properties of the initial homopolymers, particularly flame resistance and adhesivity typical of PTCB (Table XV).

A presence of 90–99% unreacted functional groups of the each type opens up a possibility for their further chemical modification. Thus, for example, the interpolymers of PTCB with PS, as well as the initial PTCB, can interact with polyethylene to form ternary interpolymers, where PTCB serves as a polymeric coupling agent between the two other polymers, PS and PEI, whose units cannot be combined in the macromolecule by other methods.⁷⁹

Concluding this section, it should be noted that all chemical reactions with PTCB are accompanied by its dehydrochlorination. However, the activation energy of PTCB dehydrochlorination (150 kJ/mol) is higher than the activation energies of the interpolymer reactions (96.1 kJ/mol for the Friedel–Crafts reaction⁶⁹ and 125 kJ/mol for the Hoffmann reaction⁵¹); therefore the reactions of allyl chlorine substitution dominate, as a rule, over the dehydrochlorination. We can reduce the side reaction of dehydrochlorination to a minimum and obtain entirely soluble

modified polymers choosing the conditions of reaction between PTCB and other macromolecular reagents (dilute solution, reduced temperature).

CONCLUSIONS

1,1,2-Trichlorobutadiene-1,3 (TCB) is readily polymerized by a radical mechanism in mass, emulsion and solution. Its polymerization rate is similar to that of chloroprene, and entirely soluble polymers are produced in the process, in contrast to chloroprene polymerization. The PTCB yield ranges from 70 to 99%, and the molecular mass from 3×10^3 to 3.5×10^6 depending on the polymerization method.

PTCB is an amorphous polymer with a glass-transition point at 55°C. PTCB contains 66–67% chlorine, which is responsible for its high adhesion and self-extinguishing properties.

PTCB dissolves in many organic solvents (aromatic and chlorinated hydrocarbons, dioxane, tetrahydrofuran); it forms transparent elastic films from solutions, the strength and deformability of which increase with increasing molecular mass (for the most high-molecular specimens the relative deformation attains about 1000%).

The PTCB structure is a combination of the units of the 1,4- and 3,4-addition in the ratio 85:15. The 1,4-units are present in *cis*- and *trans*-forms (28:72); a small admixture of the abnormal fragments consisting of the 1,4-units of head-to-head type is also observed.

In the IR spectra of PTCB there are two absorption bands (1650 and 1600 cm^{-1}) in the region of vibrations of double bonds assigned to 1,4- and 3,4-structures. The bands 2865 , 2835 and 2970 cm^{-1} in the region of vibrations of C—H bonds are assigned to the methylene-group vibrations, and the band 3080 cm^{-1} is characteristic of the —CH= group. There are three bands (720 , 760 and 780 cm^{-1}) in the region of vibrations of C—Cl bonds; the band at 720 cm^{-1} is associated with vibrations of the chlorine atoms in the allyl position to a double bond.

Protons of the 1,4-structure units manifest themselves in the NMR ^1H -spectrum as the signals 3.45 – 3.50 and 6.43 – 6.75 ppm, and protons of the 3,4-structure units, as the multiplets centered at 1.78 and 3.00 ppm.

In the NMR ^{13}C -spectrum the signals of the 1,4-structure units (87.45 – 88.23 , 136.17 – 136.82 , 124.54 – 126.84 , 46.31 – 46.34) are more intense than the signals of the 3,4-structure units (119.62 – 121.24 , 133.34 – 133.70 , 31.36 – 33.33 , 38.58 – 40.26).

We can change the ratio of the 1,4- and 3,4-structures in the PTCB molecules by carrying out the polymerization of TCB in the following ways: by a radical mechanism in the presence of some redox initiators (about 30% of 3,4-structure units); by the combined action of the shear deformation and high pressure (about 40% of 3,4-structure units); by the solid-phase polymerization under γ -radiation when the process proceeds by an ionic mechanism with the formation of the 3,4-structures predominantly. An increase in the content of the 3,4-structures in the polymer is accompanied by the increasing values of glass-transition point and thermal stability.

The PTCB properties can be modified just as in the course of the polymer

synthesis by the radical copolymerization of TCB with different vinyl monomers, as by the chemical transformations of the obtained polymer in various polymer-analogous and interpolymer reactions.

In radical copolymerization with vinyl monomers (styrene, acrylonitrile, vinylacetate, acrylic and methacrylic acids, and so on) TCB is usually more active, and therefore the copolymers are enriched, as a rule, with TCB units.

By introducing extraneous units in PTCB we can regulate its glass-transition point, the strength and elasticity of films, the resistance to thermooxidative destruction and solubility. All copolymers and the TCB-based compositions retain the inherent PTCB flame resistance and high adhesivity.

The ability of PTCB to enter into various chemical reactions both with low-molecular and high-molecular reagents of different chemical nature is attributable to the presence of the highly-mobile allyl chlorine atoms in most of its repeating units (1,4-structures).

Among the polymer-analogous reactions of PTCB the bromination, the substitution of an aromatic radical for the allyl chlorine (Friedel–Crafts reaction), and the interaction with amines (Hoffmann reaction) have been studied.

The bromination of PTCB by free bromine or bromosuccinamide results in introducing 20–25% of bromine into the polymer. The polymer structure is heterogeneous; the reaction is followed by its destruction and crosslinking. The PTCB bromination increases its glass-transition point, improves its adhesion properties and flame resistance, enhances the strength and reduces the relative deformation of the polymer films.

PTCB reacts with benzene and its homologues in the presence of Friedel–Crafts catalysts (AlCl_3 and others). The substitution of phenyl for allyl chlorine is accompanied by the allyl rearrangement in the polymer chain with a migration both of chlorine and phenyl. The degree of substitution of phenyl for chlorine ranges from 5 to 90% depending on the reaction conditions. As the degree of substitution increases, the glass-transition point, the strength of the polymer films and the polymer thermal stability increases markedly.

The reaction of PTCB with amines proceeds through a formation of the charge-transfer complexes and is completed by replacing the allyl chlorine in the polymer chain with an amino group. The intramolecular dehydrochlorination of PTCB under the effect of amine proceeds at the same time and therefore polyconjugated structures appear in the polymer. In this case, the modified PTCB is a soluble or crosslinked black-coloured product.

Very interesting polymers have been obtained in the reaction of PTCB with other high-molecular compounds, polystyrene (according to the Friedel–Crafts reaction) and polyethyleneimine (Hoffmann reaction). These reactions were carried out in solution, and completely soluble hybrid polymer systems, interpolymers, were obtained.

The interpolymer reactions proceed by the same scheme as the corresponding polymer-analogous reactions. The peculiar features of the reactions depend on the nature of both reagents, primarily, by the conformational effects of the polymer chains.

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