Phase-transfer catalysis in reactions with the participation of polyvinyl chloride*

G. V. Leplyanin★ *and V. N. Salimgareeva*

Institute of Organic Chemistry, Ufa Scientific Center of Ural Branch of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

When polyvinyl chloride is dehydrochlorinated under conditions of phase transfer catalysis, the nature of the interface determines the supramolecular structure of the synthesized polyacetylene, the packing density of crystalline regions in the polyacetylene, and the chemical properties of the polymer. The ionic mechanism of catalysis of these reactions has been established.

Key words: phase-transfer catalysis, polyvinyl chloride, polyacetylene, interface, supramolecular structure, dehydrochlorination.

Phase-transfer catalysis is widely used in reactions with the participation of high-molecular compounds, in the synthesis of polymers by polycondensation,[1,2] in polymerization of vinyl and heterocyclic monomers,[3] and in reactions of elimination, in particular, in dehydrohalogenation of halogen-containing polymers. Modification and functionalization of macromolecules are performed with the use of phase transfer catalysis. For example, aqueous solutions of nucleophiles are used for performing nucleophilic substitution in halomethylated polymers[4—11] and hydrolyzing polymethyl methacrylate.[12] Works on dehydrohalogenation of polyvinylidene chloride,[13] polyvinylidene fluoride,[14—18] a copolymer of vinylidene chloride and vinyl chloride,[19,20] and polyvinyl chloride[21—26] are available.

Elimination of hydrogen chloride from polyvinyl chloride results in a conjugated polyene structure, *trans*-polyacetylene.[21,22] Two-phase dehydrochlorination of polyvinyl chloride with the aim of preparing polyvinylacetylene is performed in the presence of ammonium or phosphonium halides with the use of a powder,[21,23] a film,[21,22] or a solution[21,23—26] of the polymer.

The traditional notion of phase-transfer catalysis implies the presence of the interface.[27,28] In this work, dehydrochlorination of polyvinyl chloride under conditions of phase transfer catalysis with the use of different bases and solvents has been studied and properties of the polyacetylene formed have been studied with the aim of obtaining knowledge on the effect of the nature of the interface on the parameters of the process and properties of the obtained product.

Experimental

Dehydrochlorination of a powder, film, and solvent of polyvinyl chloride was carried out in the presence of catalysts of interphase transfer. The reaction product was filtered off, washed with ethanol and distilled water, and dried *in vacuo*. All procedures were performed under an argon atmosphere; before using, solutions of reagents were blown with argon for 15—20 min.

Benzene, chlorobenzene, *o*-bromochlorobenzene, nitrobenzene, dichloroethane, THF, cyclohexanone, DMF, dioxane, and methyl ethyl ketone were used as the solvents for polyvinyl chloride.

The following bases were used: sodium ethoxide, lithium hydroxide, sodium hydroxide, ammonium hydroxide, and potassium hydroxide in the form of aqueous and alcoholic solutions, granules, and powders.

Either pure quaternary ammonium salts or their mixtures with alcohols were used as catalysts: tetramethylammonium iodide, tetraethylammonium iodide, tetrabutylammonium iodide, tetramethylammonium bromide, tetraethylammonium bromide, tetrabutylammonium bromide, allyltrimethylammonium bromide, tetraethylammonium chloride, triethylmethylammonium chloride, triethylbenzylammonium chloride, tetraethylammonium hydroxide, and triethylbenzylammonium benzylate.

Ethyl, *n*-octyl, benzyl, allyl, and propargyl alcohols, cyclohexanol, glycerol, and phenol were used as additives to the catalysts.

The structure of crystals obtained were studied by IR spectroscopy (on a Specord M-80 instrument), optical microscopy (an Amplival Pol. U microscope, Zeiss, Jena), and electron microscopy (an EMMA-4 electron microscope). X-ray diffraction patterns were obtained on a DRON-2 diffractometer (Cu-Kα radiation).

Thermal treatment was performed in a silica fused tube *in vacuo* (at ~10^{-3} Torr). Heating to a specified temperature was carried out at the rate of 1.5 K $\min^{-1}$; heating at this temperature was performed for 4 h.

Atmospheric oxygen and ozone were used for oxidation. Air was dried over P_2O_5. An ozone—oxygen mixture with an

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Table 1. Effects of conditions of interface dehydrochlorination of polyvinyl chloride on the supramolecular structure of polyacetylene

Phase state		Conditions	Structure of polyacetylene
Polyvinyl chloride	KOH		
Powder	Aqueous solution (50 %)	Stirring	Polyacetylene is absent
Swollen in nitrobenzene	«	Steady-state conditions	Amorphous
«	«	Active washing of a film with a KOH solution	Crystalline
Solution in tetrahydrofuran	«	Stirring	Amorphous + 20 % of a crystalline modification
Solution in tetrahydrofuran	«	Steady-state conditions	Amorphous
Solution in nitrobenzene	«	Steady-state conditions	Amorphous with an admixture of crystals
«	«	Stirring	Perfect crystals
«	Powder	«	Amorphous + 20 % of a crystalline modification
Solution in nitrobenzene	Solution in ethanol (25 %)	«	«

Note. The duration of the reaction is 7 h.

ozone concentration of 1—2 vol. % was passed at room temperature at the rate of 2—5 L h^{-1} through the tube (7×0.5 cm) filled with polyacetylene.

Results and Discussion

Effect of the nature of the interface on dehydrochlorination of polyvinyl chloride. Dehydrochlorination of polyvinyl chloride proceeds in two-phase systems: solid—liquid and liquid—liquid. The structure of the interface affects the supramolecular structure of the formed polyacetylene, *i.e.*, the mode of packing of macromolecules in spatially separated elements, the size and shape of these elements, and their mutual spatial arrangement.

When the reaction is performed in a solid—liquid system (a film, a powder of polyvinyl chloride—a solution of a base, or a solution of polyvinyl chloride—a powder of a base), chaotically arranged macromolecules, which are located in near-surface regions, are subjected to dehydrochlorination; obtained polyacetylene has an amorphous structure (Table 1). In a liquid—liquid system (a solution of polyvinyl chloride—a solution of a base), the degree of conversion of polyvinyl chloride (Table 2) and the reaction rate (Fig. 1) depend only slightly on the nature of a solvent. The exceptions are solvents capable of reacting with the base (KOH) — DMF and dichloroethane.

Apparently, in these cases, the concentration of the base in the reaction zone, *i.e.*, at the interface, is reduced as a result of competing reactions (a solvent—KOH and polyvinyl chloride—KOH); this leads to a substantial decrease in the rate of the main process.

When the reaction is performed with a solution of polyvinyl chloride in water-miscible solvents, the supramolecular structure (crystallinity) of polyacetylene is independent of the nature and polarity of the solvents. In all cases, mixtures of amorphous polyacetylene with

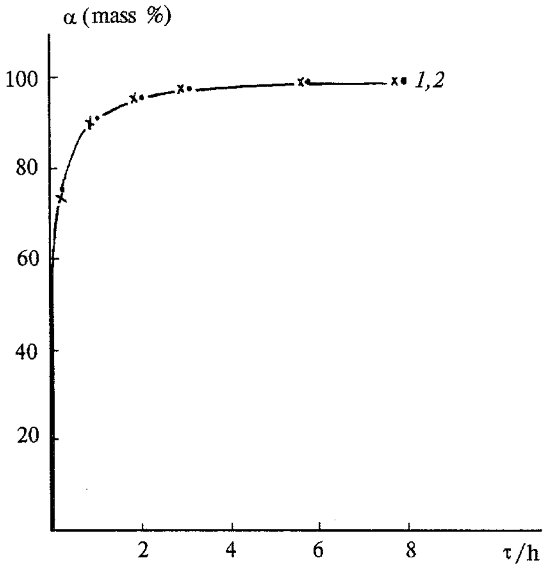

Fig. 1. Kinetic curves of dehydrochlorination of polyvinyl chloride with a 50 % KOH solution in nitrobenzene (*1*) and methyl ethyl ketone (*2*) at T = 293 K. [KOH] = 0.41 g per mL of the organic phase, [triethylbenzylammonium chloride] = $2.8 \cdot 10^{-2}$ mol per unit of polyvinyl chloride, [triethylbenzylammonium chloride] : [benzyl alcohol] = 1 : 6.3 (mol mol^{-1}), [polyvinyl chloride] = 1.5 mass %, α is the degree of conversion.

Table 2. Effect of the nature of solvents on dehydrochlorination of polyvinyl chloride with the 50 % KOH aqueous solution

Solvent	Miscibility of solvent with water	ε	[Polyvinyl chloride] (mass %)	[KOH] /g mL^{-1}	Degree of conversion (%)	Structure of polymer
THF	Miscible	7.39	1.50	0.42	98	Amorphous + 20 % of a hexagonal modification
Cyclohexanone	Miscible	18.30	«	«	96	«
DMF	Miscible	37.60	«	«	38	«
Dioxane	Miscible	2.20	«	«	92	«
Methyl ethyl ketone	Miscible	18.50	«	«	95	«
Benzene	Immiscible	2.27	0.10	0.05	0	No
Chlorobenzene	Immiscible	6.08	0.78	0.05	80	Amorphous
Dichloroethane	Immiscible	10.36	1.50	0.42	35	Amorphous + 20 % of a hexagonal modification
Nitrobenzene	Immiscible	34.75	1.50	0.42	98	Perfect crystals
Nitrobenzene	Immiscible	«	0.78	0.05	80	«
o-Bromochlorobenzene	Immiscible	10.00	1.50	0.42	90	Amorphous + finely crystalline

Note. $T = 298$ K, $\tau = 7$ h, [triethylbenzylammonium chloride] : [benzyl alcohol] = 1 : 6.3 (mol mol^{-1}).

crystalline polyacetylene (up to 20 % of the latter) are formed. In water-immiscible solvents, the structure of obtained polyacetylene is determined by the polarity of a medium (ε). In solvents with a low dielectric permeability ($\varepsilon \leq 6$), only an amorphous structure occurs; in solvents with a higher polarity ($\varepsilon \sim 10$), a mixed structure, which consists of an amorphous polymer with the inclusion of up to 20 % of finely crystalline structures, is observed. Polyacetylene, which is obtained in a solvent with $\varepsilon \sim 30$, consists of single crystals. Apparently, a water-immiscible polar solvent favors the formation of a clearly defined interface, separation of charges, and their simultaneous orientation parallel to the surface of the interface.

Molecules of polyvinyl chloride in a solution are one-dimensional cooperative systems, in which intramolecular interactions between units of the chain are stronger than intermolecular interactions. On dehydrochlorination, flexible segments of macromolecules of polyvinyl chloride are converted to one-dimensional rigid polyconjugated structures; in the case of immiscible phases, these structures are oriented parallel to the interface, which is favorable for drawing off subsequent segments of the macromolecule from the solution to the reaction zone. Interchain interactions of polyene fragments lead to two-dimensional systems. The rigidity of polyconjugated structures prevents an arrangement of macromolecules in which amorphous regions may be buried in a large body of superimposed chains. As a result, a three-dimensional system occurs with the formation of stack crystals of a regular shape, which are observed in polarization-optical studies. Three modifications of crystals of polyacetylene were identified by electron diffraction analysis: hexagonal ($a = b = 5.2$ Å, $c = 2.52$ Å), orthorhombic ($a = 4.0$ Å, $b = 7.9$ Å, $c = 2.52$ Å), and monoclinic ($a = c = 3.9$ Å, $b = 2.52$ Å) modifications.

Crystalline polyacetylene is synthesized only by the reaction proceeding at the interface. Photomicrographs of the interface (Fig. 2) show that under steady-state conditions the process starts at the interface (Fig. 2, *a*) and then spreads over the bulk of the organic phase (Fig. 2, *b*). Apparently, the crystal structure is formed only when diffusion of reagents occurs in a viscous sublayer (near the interface), while diffusion through the interface (transport of reagents from one phase to another) hinders crystallization of the polymer. Therefore, under steady-state conditions, a crystalline polymer is not formed (except for a thin film at the interface) regardless of the form in which the initial polyvinyl chloride is used: a solution in nitrobenzene or a film swollen in nitrobenzene (see Table 1). Only under dynamic (turbulent) conditions, the process affords the crystal structure. Stirring causes a mechanical increase in the surface of the interface and, therefore, determines the orientation of a large number of molecules of polyvinyl chloride along the interface. Furthermore, because of an increase in the reaction rate on stirring, the process occurs in a viscous sublayer, and the reagents have not managed to pass into the organic phase.

As observations of the reaction under steady-state conditions with the use of an universal microscope show, when water-miscible solvents are used, dehydrochlorination starts simultaneously at the interface (intensively) and over the bulk of the organic phase (less intensively). Although the miscibility of organic com-

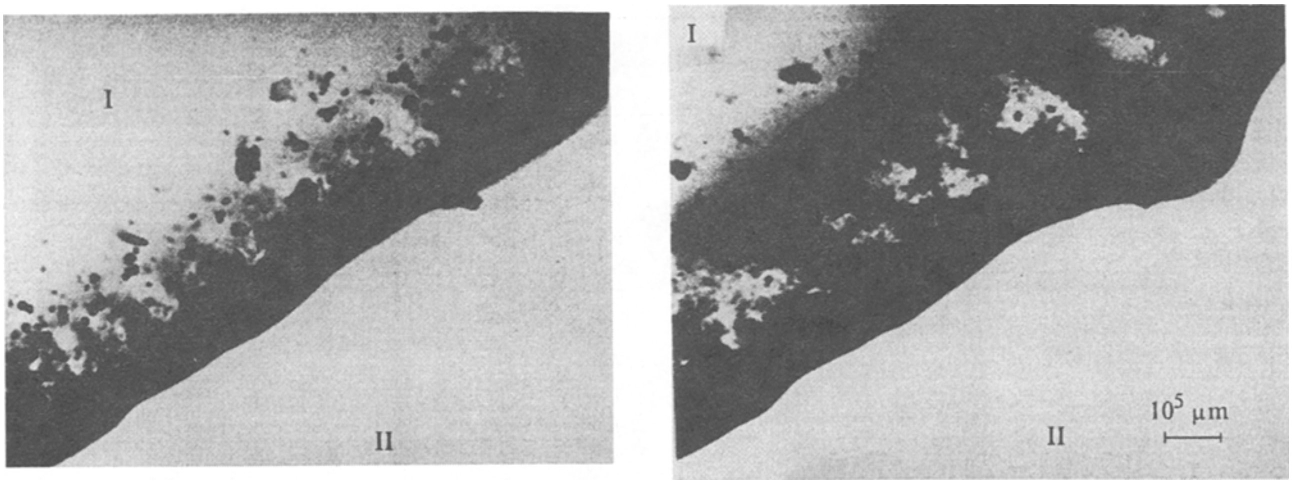

Fig. 2. Photomicrographs of the interface between nitrobenzene (I)—a 50 % KOH solution (II) upon dehydrochlorination of polyvinyl chloride. The catalytic system: triethylbenzylammonium chloride—benzyl alcohol (1 : 6.3, mol mol^{-1}). Within 10 s (*a*) and 25 s (*b*) after the beginning of the reaction.

pounds and concentrated aqueous solutions of alkalis is small, it is sufficient for the reaction to proceed in the bulk of the organic phase. Apparently, an extended indistinct interface hinders the orientation of molecules of polyvinyl chloride along the interface and the ordered packing of the formed macromolecules of polyacetylene in the crystal. Because of the absence of a distinct interface, dehydrochlorination of polyvinyl chloride with an aqueous KOH solution in water-miscible solvents and dehydrochlorination with an alcoholic KOH solution in water-immiscible but alcohol-miscible solvents are identical (Tables 2 and 3): the degrees of conversion of the polymer are close, and the supramolecular structures of the obtained polyacetylene are identical.

Therefore, the interface, which is determined by the nature of the solvent, base, turbulent or steady-state conditions of the process, affects the supramolecular structure of polyacetylene synthesized by dehydrochlorination of polyvinyl chloride. Dehydrochlorination with an aqueous KOH solution in polar water-immiscible solvents affords highly crystalline polyacetylene; in this case, the crystal dimensions substantially exceed those reported in the literature: dimensions can be as much as $1.0 \cdot 10^{-3}$ μm. The polyacetylene, obtained by polymerization of acetylene, is characterized by a fibrillar structure; the average sizes of the fibrils are 200—500 Å.[29]

Effect of the nature of a catalytic system on the process of dehydrochlorination of polyvinyl chloride. The function

Table 3. Effect of the nature of the base on dehydrochlorination of polyvinyl chloride

Base	Concentration of the used solution (%)	Degree of conversion (%)	Structure of polymer
C_2H_5ONa[a]	100	34	Amorphous
C_2H_5ONa[b]	«	67	«
KOH in ethanol	25	90	Amorphous + 20 % of a hexagonal modification
KOH[b]	100	98	«
NH_4OH[c]	30	0	Polymer is absent, τ = 40 h
LiOH[c]	60 g/100 g H_2O	58	Fine crystalline + amorphous
NaOH[c]	50	96	Imperfect crystals
KOH[c]	30	84	Highly crystalline
KOH[c]	50	97	Perfect crystals

Note. [Polyvinyl chloride] = 1.5 mass %; [triethylbenzyl alcohol] = $5.1 \cdot 10^{-2}$ mol per unit of polyvinyl chloride; [triethylbenzylammonium chloride] : [benzyl alcohol] = 1 : 6.3 (mol mol^{-1}). The concentration of the base is 0.42 g per mL of the organic phase, T = 298 K, τ = 7 h.
[a] Powder; without a catalyst. [b] Powder. [c] Aqueous solution.

Table 4. Effect of the nature of quaternary ammonium salts on dehydrochlorination of polyvinyl chloride

Catalyst	Without additives		With addition of benzyl alcohol in the ratio of 1 : 6.3 (mol mol^{-1})	
	Degree of conversion (%)	Structure of polymer	Degree of conversion (%)	Structure of polymer
Tetramethylammonium iodide	0	—	0	—
Tetraethylammonium iodide	30	Amorphous + finely crystalline	83	Finely crystalline + amorphous
Tetrabutylammonium iodide	37	«	84	Imperfect crystals
Tetramethylammonium bromide	48	«	93	«
Tetraethylammonium bromide	87	Finely crystalline + amorphous	97	«
Tetrabutylammonium bromide	86	«	90	«
Allyltrimethylammonium bromide	63	«	72	«
Tetraethylammonium chloride	87	Finely crystalline	98—99	«
Triethylmethylammonium chloride	94	Finely crystalline	92	«
Triethylbenzylammonium chloride	75	Crystalline + amorphous	98—99	Perfect crystals
Tetraethylammonium hydroxide	88	Finely crystalline + amorphous	49.5	Amorphous
Dibenzo-18-crown-6	45	Crystals + amorphous	—	—
Triethylbenzylammonium benzylate	96	Imperfect crystals	—	—
Triethylbenzylammonium chloride + $C_6H_5CH_2ONa$	73	Finely crystalline + amorphous	—	—

Note. [Polyvinyl chloride] = 1.5 mass %, [KOH] = 0.41 g per mL of the organic phase, [quaternary ammonium salt] = $5 \cdot 10^{-2}$ mol per unit of polyvinyl chloride, T = 298 K.

of catalysts in two-phase reactions is to form ionic pairs (a cation of a catalyst—a reacting anion) capable of associating and migrating into an organic phase.[30]

When polyvinyl chloride is dehydrochlorinated in nitrobenzene with an aqueous KOH solution (Table 4), catalytic activity of crown ethers is low: the degree of conversion is no more than 45 %. Evidently, catalysis occurs not through binding of K^+ cations with the formation of complexes.

An increase in the length of the carbon chain of the cation of quaternary ammonium salts results in an enhancement of its lipophilicity and an increase in the degree of conversion. Quaternary ammonium salts, which contain benzyl groups, ranks below quaternary ammonium salts with alkyl groups in catalytic properties, apparently, due to a higher hydrophilicity.

At low concentrations of quaternary ammonium salts in solvents with a high dielectric permeability, ionic pairs primarily dissociate into ions. The larger the size of the ion, the higher the degree of dissociation.[31,32] In highly polar nitrobenzene, catalysts with a bulky or a long carbon chain of a cation occur, apparently, in the form of free ions.

The nature of the anion of quaternary ammonium salts also plays an important role in these reactions. When the cationic parts are identical, the catalytic activity of tetraalkylammonium halides in dehydrochlorination of polyvinyl chloride changes in the following order: $I^- < Br^- = Cl^-$. The activity of quaternary ammonium salts is not connected with the lipophilicity of halides, which decreases in the following series: $I^- > Br^- > Cl^-$ (see Ref. 33) and is determined, apparently, by the sizes of the anions. The large iodine anion compared to chlorine and bromine anions (their radii are 2.20 Å, 1.81 Å, and 1.96 Å, respectively[34]) favors a decrease in adsorption of iodine at the interface.

Supramolecular structures of polyenes, which are obtained in the presence of tetraalkylammonium chlorides and tetraalkylammonium bromides are virtually identical; polyenes are in the form of a finely crystalline modification with an admixture of an amorphous component. The exception is triethylbenzylammonium chloride, in the presence of which crystalline polyene is formed (crystal dimensions are up to 10 μm); when other quaternary ammonium salts are present, the dimensions of the crystals formed are no larger than 1 μm.

Apparently, the reason is that an interaction of triethylbenzylammonium chloride with the aqueous phase is stronger compared to the interaction between salts with aliphatic radicals and the aqueous phase due to the enhanced hydrophilicity of triethylbenzylammonium chloride compared to hydrophilicity of other salts.[28] Addition of alcohols to triethylbenzylammonium chloride increases the degree of conversion (Table 5). In the presence of alcohols, an alkoxide anion, which is a strong base, acts as a nucleophilic agent.[35] The catalytic activity of triethylbenzylammonium chloride is unaffected by phenol. The nature of the added alcohol has no effect on the degree of conversion, which is equally high on dehydrochlorination of polyvinyl chloride in the presence of triethylbenzylammonium chloride with addition of saturated monohydric (ethanol and octanol), unsaturated (allyl and propargyl alcohols), polyhydric (glycerol), aromatic (benzyl alcohol), and acyclic (cyclohexanol) alcohols.

However, the nature of alcohols in this catalytic system affects the supramolecular structure of polyacetylene formed. Addition of alcohols with bulky substituents at the hydroxyl group (cyclohexanol, glycerol, and benzyl alcohol) results in formation of polyene, the structure of which is a combination of crystalline and amorphous portions with different degrees of ordering. In this series, the system, which consists of triethylbenzylammonium chloride with an addition of benzyl alcohol, stands out. In the presence of this additive, single crystals of polyacetylene are formed; the crystal dimensions are $(0.3-1.0)\cdot10^3$ μm. In the case of other alcohols, the crystal structure is imperfect and the crystals are very small.

Table 5. Effect of addition of alcohols on the catalytic activity of triethylbenzylammonium chloride upon dehydrochlorination of polyvinyl chloride with 50 % KOH solution

Alcohol as an additive	Degree of conversion (%)	Structure of polymer
—	85	Finely crystalline + amorphous
Ethanol	94	«
n-Octanol	92	«
4-Methylcyclohexanol	99	Crystalline + finely crystalline
Glycerol	99	Crystalline + amorphous as an admixture
Allyl alcohol	99	Amorphous + finely crystalline
Propargyl alcohol	99	Crystalline + finely crystalline
Phenol	83	Finely crystalline + amorphous
Benzyl alcohol	99	Perfect crystals

Note. [Polyvinyl chloride] = 1.5 mass %, [KOH] = 0.42 g per mL of the organic phase, [triethylbenzylammonium chloride] = $5\cdot10^{-2}$ mol per unit of polyvinyl chloride, [triethylbenzylammonium chloride] : [alcohol] = 1 : 6.3 (mol mol^{-1}), T = 293 K, τ = 7 h.

The promoting role of benzyl alcohol is observed on dehydrochlorination of polyvinyl chloride in the presence of other quaternary ammonium salts as well (see Table 4).

Perfect crystals are formed in the presence of the catalytic triethylbenzylammonium chloride+benzyl alcohol system.

To obtain highly crystalline polyene, the presence of all the components of the catalytic system (*i.e.*, the presence of a quaternary ammonium salt, alcohol, and products of their interaction) is required. Dehydrochlorination of polyvinyl chloride in the presence of triethylbenzylammonium benzylate does not afford perfect crystals, although the reaction proceeds with a high degree of conversion (see Table 4). When catalysis is carried out with an equimolar mixture of sodium benzylate and triethylbenzylammonium chloride, the degree of conversion is equal to that obtained in the presence of triethylbenzylammonium chloride. Apparently, triethylbenzylammonium benzylate is not formed in the reaction mixture of these compounds. A

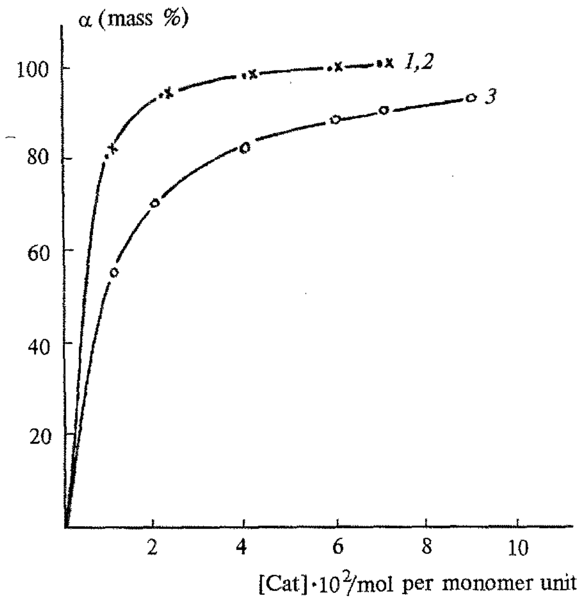

Fig. 3. Relationship between the degree of conversion and the concentration of the catalyst when the base is used at the following concentrations: *1*, 0.84 g per mL of the organic phase; *2*, 0.42 g per mL of the organic phase; *3*, 0.05 g per mL of the organic phase. The solvent is nitrobenzene, [polyvinyl chloride] = 1.5 mass %. T = 301÷303 K.

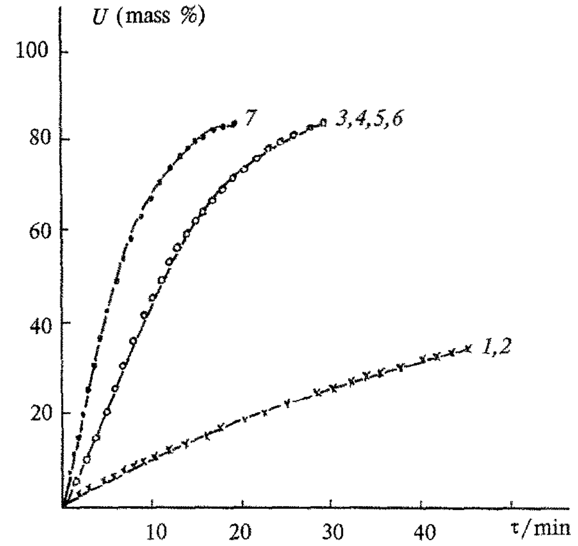

Fig. 4. Kinetic curves obtained upon dehydrochlorination of 1,2-dichloroethane with a 50 % KOH aqueous solution at T = 313 K (*1, 2, 3, 4, 5,* and *6*) and 323 K (*7*). [Dichloroethane] : [KOH] = 1 : 3 (mass %). *1*, [triethylbenzylammonium chloride] = $3.60 \cdot 10^{-2}$ mol L^{-1}; *2*, triethylbenzylammonium chloride , irradiation with ultraviolet light; *3*, triethylbenzylammonium chloride+benzyl alcohol (1 : 6.3, mol mol^{-1}); *4*, [triethylbenzylammonium chloride+azaisobutyronitrile] = $3 \cdot 10^{-2}$ mol L^{-1}; *5*, [triethylbenzylammonium chloride+dicyclohexyl percarbonate] = $5.4 \cdot 10^{-2}$ mol L^{-1}; *6*, triethylbenzylammonium chloride, irradiation with ultraviolet light; *7*, triethylbenzylammonium chloride+benzyl alcohol (1 : 6.3, mol mol^{-1}).

concentration of a catalyst affects the degree of conversion (Fig. 3) but does not change the structure of the polymer: dehydrochlorinated fragments in the polymer are characterized by crystallinity.

Effect of the nature of the base and the temperature of the process on dehydrochlorination of polyvinyl chloride. The nature of the base and its concentration affect the reaction rate and crystallinity of the product formed (see Table 3). When strong bases (KOH and NaOH) are used, the reaction proceeds with high conversion. The equal activity of these bases is determined by close values of affinity for proton of these molecules.[36] When KOH is used, the crystal structure of obtained polyacetylene is more perfect compared to that obtained with the use of NaOH. This is attributable to the possibility of the more active stirring if KOH is used because of a lower viscosity of its 50 % aqueous solution compared to a NaOH solution.[37] The reaction temperature has no affect on the final degree of conversion but substantially affects the crystallinity of the polyacetylene formed. In the temperature range 280—303 K, a perfect crystal structure is formed; an increase in temperature to 323 K leads to the synthesis of imperfect opaque crystals.

Mechanism of dehydrochlorination of polyvinyl chloride. Figure 4, in which kinetic curves of the model reaction of dehydrochlorination of 1,2-dichloroethane in the presence of triethylbenzylammonium chloride with and without the addition of benzyl alcohol are presented, shows that this additive substantially increases the reaction rate (curves *1* and *3*). Irradiation of the reaction mixture with ultraviolet light and peroxide initiators (dicyclohexyl percarbonate and azaisobutyronitrile) have no effect on the rate of the reaction, which proceeds in the presence of the triethylbenzylammonium chloride+benzyl alcohol catalytic system.

Dehydrochlorination of polyvinyl chloride occurs in nitrobenzene, which is an inhibitor of radical processes.[38] The use of nitrobenzene in large quantities renders dehydrochlorination by a radical mechanism impossible. The kinetic curves of dehydrochlorination of polyvinyl chloride in nitrobenzene and methyl ethyl ketone (which is not an inhibitor of radical reactions), which are shown in Fig. 1, coincide, which points to the fact that this is not a radical process. This conclusion is also confirmed by the fact that neither introduction of an additional inhibitor, hydroquinone, in large quantities (10 mass % with respect to polyvinyl chloride) to the reaction mixture nor irradiation of the reaction mixture with ultraviolet light affects the degree of conversion.

Therefore, dehydrochlorination of polyvinyl chloride under conditions of phase transfer catalysis in the presence of quaternary ammonium salts occurs at the interface by a ionic mechanism. The interface determines a supramolecular structure of the synthesized polymer and its physical and chemical properties.

Structure and physical properties of polyacetylene. The conditions of synthesis of polyacetylene by interface dehydrochlorination of polyvinyl chloride have no effect on the configuration of the polyacetylene molecules. The IR spectrum is characterized by the presence of bands at 1292, 1000—1015, and 3010—3015 cm^{-1}, corresponding to in-plane and out-of-plane bending and stretching =C—H vibrations in the *trans* configuration.

The pycnometric density of amorphous polyacetylene is 0.78 g cm^{-3}. The density of crystalline samples depends on the concentration of the KOH solution, which is used in dehydrochlorination of polyvinylchloride. When a 50 % solution is used, the polymer with the density $d = 1.15\div1.20$ g cm^{-3} is formed; when the KOH concentration in the solution is lower (20—30 %), the density of the polymer is $d = 1.30\div1.35$ g cm^{-3}. An analogous phenomenon is also observed under changes of the concentration of KOH in the organic phase when a 50 % solution is used. At the KOH concentration of 0.42 g mL^{-1}, the polymer with $d = 1.15\div1.20$ is formed; at a concentration of 0.25 g mL^{-1}, the polymer with $1.30\div1.35$ g cm^{-3} is formed.

A substantial difference is observed in X-ray diffraction patterns of crystalline and amorphous samples (Fig. 5, curves *1*, *3*, and *4*); this difference is characterized by an almost twofold increase in intensity of the peak at $2\theta \approx 20$—25° in crystalline polyacetylene compared to amorphous polyacetylene, It turns out that X-ray diffraction patterns of crystalline polyacetylene samples with different pycnometric densities do not differ from each other: positions of peaks and intensities are identical (see Fig. 5, curves *1* and *3*). Therefore, the X-ray densities of these samples are equal. The difference in densities determined by X-ray diffraction analysis and the pycnometric method is attributable to different concentration of closed pores.[39] With identical X-ray diffraction density, the porosity is smaller in samples with a high pycnometric density.

When KOH with concentrations of 0.42 g mL^{-1} and 0.25 g mL^{-1} is used in the organic phase, the reaction rates of dehydrochlorination are different, though the densities of synthesized polymers are equally high. When the reaction proceeds for 7 h, the degree of conversion is 73 % and 97 % in the first and second cases, respectively. Apparently, the porosity and defects of the structure are determined not by the reaction rate but by the structure of the interface.

Crystallinity and micropore volume in samples affect chemical properties of the polymer: stability to a high temperature and oxidants.

Chemical properties of polyacetylene. The rigid crystal packing of macromolecules determines an anomalously low thermal stability. Dehydrogenation starts even at 520 K, which affords completely carbonated samples (1500—1700 K) through a series of intermediate structures. Curves of the dependence of the C/H ratio, which characterizes the degree of hydrogen loss with temperature (Fig. 6) show that crystalline polyacetylene (curve *1*) is dehydrogenated at a higher rate than amorphous polyacetylene (curve *2*). The amorphous polymer is completely carbonated only at the temperature higher than 2300 K. It turns out that the capability of crystalline

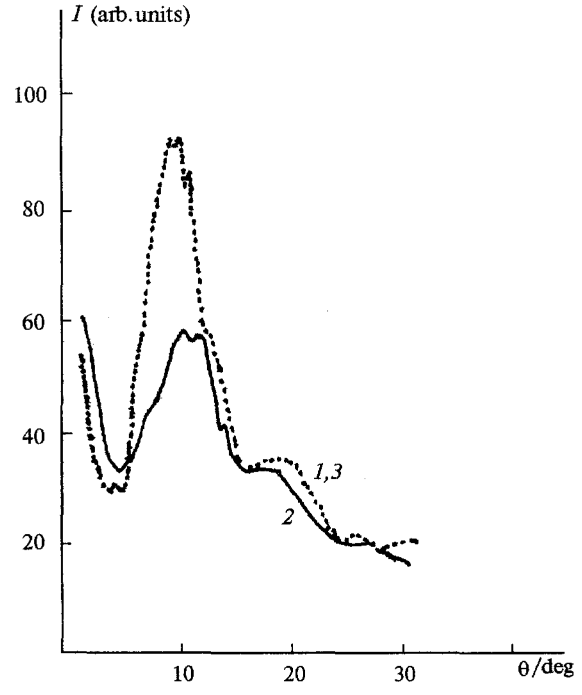

Fig. 5. X-ray diffraction patterns of samples of crystalline (*1* and *3*) and amorphous (*2*) polyacetylene. The densities of the crystalline polyacetylene are 1.15 g cm^{-3} (*1*) and 1.35 g cm^{-3} (*3*).

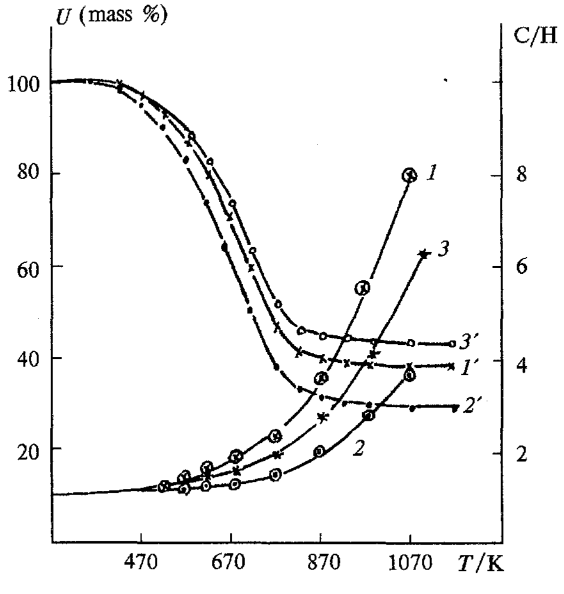

Fig. 6. Relationship between the C/H ratio (*1*, *2*, and *3*) and the weight loss (*1′*, *2′*, and *3′*) of crystalline (*1*, *1′*, *3*, and *3′*) and amorphous (*2* and *2′*) polyacetylene. The densities of the crystalline polyacetylene are 1.15 g cm^{-3} (*1* and *1′*) and 1.35 g cm^{-3} (*3* and *3′*).

Table 6. Results of the reaction of polyacetylene with ozone

Structure of polymer	Solvent in the synthesis of polyacetylene	*d* /g cm^{-3}	Action of ozone	
			combustion[a]	increase in weight[b]
Amorphous + fine crystalline	THF	0.78	+	–
«	Methyl ethyl ketone	0.76	+	–
«	Dioxane	0.76	+	–
Perfect crystals	Nitrobenzene	1.15	+	–
«	Nitrobenzene	1.20	+	–
«	Nitrobenzene	1.35	No	5 %

[a] When ozone is brought into contact, flares up immediately. [b] An increase in weight after passing ozone through the polymer for 5 h.

polyacetylene to eliminate hydrogen depends on the crystal packing density, which is indirectly characterized by the pycnometric density. In the polymer with a high density, hydrogen evolution is hindered: the curve of the temperature dependence of dehydrogenation for polyacetylene with the density of 1.35 g cm^{-3} lies lower than the curve for the sample with the density of 1.15 g cm^{-3} (curves *1* and *3*, respectively). Apparently, an enhanced thermal stability of polyacetylene with a high density is determined by the hindrance of hydrogen diffusion in extremely close packings as well as by formation of hydrogen bonds between molecules.

In crystalline polyacetylene, thermal destruction of macrochains, which proceeds with a pronounced weight loss, occurs less readily compared to thermal destruction in amorphous polyacetylene (see Fig. 6). Crystalline polyacetylene with a high density split out fragments of macromolecules more slowly than polyacetylene with a lower density (curve *3'* lies higher than curve *1'*, see Fig. 6).

The structure of polyacetylene affects its stability to oxidants (atmospheric oxygen and ozone). An increase in weight of amorphous polymer through an addition of atmospheric oxygen amounts up to 2.3 % during 24 h. The susceptibility of crystalline polyacetylene to oxidation depends on its density. The sample with the pycnometric density of 1.15—1.20 g cm^{-3} reacts with atmospheric oxygen less actively than amorphous polyacetylene: an increase in weight is 0.6 mass %. In an ozone—oxygen mixture, this sample ignites as well as amorphous polyacetylene (Table 6). Crystalline polyacetylene with a density of 1.30—1.35 g cm^{-3} does not react with atmospheric oxygen and reacts only weakly with ozone.

Apparently, oxidation is controlled by diffusion of gas oxidant in a sample. Diffusion is hindered in samples of the polymer with a high density.

Therefore, the interface exerts the determining effect on the supramolecular structure, crystallinity, concentration of micropores, and, ultimately, on crystal packing density of crystalline portions of polyacetylene, which was obtained by two-phase dehydrochlorination of polyvinyl chloride. The interface also determines chemical properties of the polyacetylene.

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