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Deformation of styrene—divinylbenzene copolymers and hypercrosslinked polystyrenes during solvent adsorption and desorption

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An automated procedure was developed for monitoring fast changes in the size of spherical samples of polymers during their contact with a solvent or drying. The kinetics of bulk deformation in these processes was studied for a series of cross-linked polymers, *viz.*, gel-type and porous styrene—divinylbenzene copolymers and poly(divinylbenzenes), and hypercrosslinked polystyrenes. Gel, macroporous, and hypercrosslinked polystyrenes are substantially different in the rate, mechanism, and degree of swelling, which is associated with the principal differences in their physical structures. An unusual effect of a sharp decrease followed by a temporary increase in the volume of porous polystyrene and poly(divinylbenzene) materials were observed during desorption (evaporation) of organic solvents. Water desorption is accompanied by an excessive bulk compression of porous granules giving rise to negative deformations, which gradually relax to the state equilibrium for the dry polymer. The results of dynamic desorption porometry (for water desorption) are indicative of a bimodal size distribution of micropores in hypercrosslinked polystyrene.

Key words: polymer swelling, bulk deformation, desorption, styrene copolymers, poly(divinylbenzene), hypercrosslinked polystyrene, porous polymers.

Swelling of cross-linked polymers in solvents can be studied by different experimental methods, which detect changes in either the weight[1—6] or the size of samples.[7—9] Methods of NMR,[10] ESR, UV, and IR spectroscopy[6] are more rarely used to study changes in other properties of systems caused by polymer swelling. A special dilatometric technique based on the monitoring of the volume of the sorbent layer in a solvent-washed cylindrical cell was described.[11] The swelling pressure and the kinetics of bulk swelling of vulcanized rubbers in different aliphatic and cyclic hydrocarbons were investigated.[6,12] Most of known methods cannot be used for studying fast changes in the geometric sizes of liquid-contacting materials. However, these data are necessary for optimization of various technological processes, particularly, of sorption processes.

In this connection, the aim of the present study was to investigate fast deformations of individual granules of cross-linked polystyrene-type polymers during solvent absorption and desorption. We studied samples of three main types of polystyrene networks, *viz.*, nonporous gel-type styrene—divinylbenzene copolymers, macroporous styrene—divinylbenzene copolymers, and macroporous poly(divinylbenzenes), and hypercrosslinked styrene copolymers,[13,14] which predominantly have a microporous structure.

Experimental

Known cross-linked polystyrene-type polymers are similar in the chemical composition and properties but differ in the structure of the polymer matrix and the pore structure. Due to this, cross-linked polystyrenes, such as nonporous copolymers, macroporous copolymers, macroporous poly(divinylbenzenes), and hypercrosslinked copolymers, differ in the main physical properties (Table 1).

Gel-type nonporous copolymers were prepared by suspension free-radical polymerization of styrene with divinylbenzene in an aqueous medium.[14] Nonporous copolymers are denoted SD1.4, SD2.7, *etc.*, where S is styrene, D is divinylbenzene, and the numbers correspond to the percentage (wt.%) of divinylbenzene in the copolymer. These polymers have a density of amorphous polystyrene and are nonporous (see Table 1).

Macroporous styrene—divinylbenzene copolymers and macroporous poly(divinylbenzenes) were synthesized analogously with the use of pore-forming solvents (toluene or hep-

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Table 1. Physicochemical properties of gel and porous styrene—divinylbenzene copolymers, poly(divinylbenzenes), and hypercrosslinked polystyrene networks*

Polymer	d_{app} /g cm^{-3}	S_{in} /m^2 g^{-1}	E_{sw} /MPa	a_s/mL g^{-1}		Q/v v^{-1}		Swelling time/s	
				Ethanol	Toluene	Ethanol	Toluene	Ethanol	Toluene
SD1.4	1.05	0	1	0	2.50	1.00	3.30	—	1200
SD2.7	1.05	0	3	0	1.70	1.00	2.50	—	1300
SD5.3	1.05	0	12	0	1.02	1.00	1.80	—	8700
SD15	1.05	0	320	0	0.48	1.00	1.40	—	—
SD15T	1.05	0	80	0.07	0.66	1.00	1.61	—	~5000
SD15H	0.68	70	80	0.63	1.29	1.03	1.40	50	30
DT	0.77	450	540	0.70	0.73	1.22	1.32	250	120
DH	0.71	580	400	0.87	0.94	1.08	1.13	20	11
XAD-4	0.52	900	200	1.36	1.40	1.22	1.23	45	19
CPS-25	1.05	0	3	0.3	2.3	1.05	3.05	—	3700
CPS-43	0.88	90	9	1.6	2.3	2.40	2.90	2300	190
CPS-66	0.77	750	16	2.5	2.8	2.45	2.60	130	44
CPS-100	0.72	1000	27	2.7	3.0	2.60	2.60	116	44
CPS-150	0.71	1300	42	3.0	3.0	2.60	2.60	80	40
CPS-200	0.74	1300	55	3.0	3.0	2.60	2.60	80	40

* d_{app} is the apparent density, S_{in} is the specific surface area, E_{sw} is the modulus of elasticity, a_s is the weight swelling, and Q is the degree of swelling.

tane), which were added to the reaction mixture in an amount of 60% w/w of the monomer mixture. These ratios were 65 and 80% v/v of the monomer mixture for toluene and hexane, respectively, when converted to the volume of the porogen. Macroporous polymers are denoted SD15H and SD15T, which correspond to styrene—divinylbenzene copolymers (15 wt.%) synthesized in the presence of heptane or toluene, respectively; DH and DT correspond to poly(divinylbenzenes) synthesized in the presence of heptane or toluene, respectively.

The polymer SD15T, though prepared in the presence of toluene, appeared to be a gel-type nonporous polymer. Granules of this polymer are mechanically stable and optically transparent. The polymers SD15H and DH, which were synthesized in the presence of heptane, are characterized by a low apparent density and a high specific surface area (particularly, the polymer DH). Granules of these polymers are milk-white in color and are mechanically less stable. Unlike the gel polymer SD15T, poly(divinylbenzene) DT, which was also prepared in the presence of toluene, is a porous material with a high specific surface area and a low apparent density (see Table 1).

In addition to the synthesized macroporous poly(divinylbenzene)-type polymers, we studied the commercial styrene—divinylbenzene copolymer Amberlite XAD-4 (Rohm & Haas), whose porous structure is formed by macro- and mesopores.

Hypercrosslinked polystyrenes were prepared by cross-linking of a granular maximum swollen styrene—divinylbenzene copolymer in dichloroethane with the use of different amounts (from 0.2 to 1.0 mol per mole of polystyrene) of monochlorodimethyl ether according to a procedure described earlier.[15] This cross-linking agent introduces methylene bridges between the Ph groups of two polystyrene chains of the starting lightly cross-linked copolymer. The hypercrosslinked copolymers are denoted CPS-25, CPS-43, *etc.*, where CPS is cross-linked polystyrene, and the numbers correspond to the formal degree of cross-linking, *i.e.*, the percentage of bridges with respect to the number of structural elements of the final network. Hypercrosslinked polystyrenes are dense polystyrene networks with loose and mobile structures.[14,16] These polymers are optically transparent and have a low density and a developed system of micropores with a huge apparent inner surface (up to 1300 m^2 g^{-1}, see Table 1).

All copolymers and hypercrosslinked polystyrenes were prepared as spherical granules of sizes from ~0.2 to 2 mm.

The specific surface area of polymers S_{in} was determined by thermal desorption of argon;[17] the apparent density d_{app}, by mercury densitometry and from the ratio of the weight to the total volume of 70—100 spherical granules (the diameter of the granules was measured under a microscope).

The swelling kinetics was studied by dilatometry on a UIP-70 instrument for thermomechanical studies of polymers. A sample granule of a regular spherical shape with a diameter from 0.6 to 0.7 mm, which was measured with an accuracy of 1 μm, was placed in a hole (radius was 1.0 mm and the depth was 0.2 mm) specially bored in a quartz plate. The changes in the granule size were monitored using a sliding quartz plunger connected to a capacity detector of the instrument and a watch-type micrometer. The plunger with a polished planar end face (diameter was 2.7 mm) touched a sample with a minimum load of 0.5 g. It has been preliminarily found that this load is much smaller than the swelling pressure of the polymers under study and does not cause deformations of the fully swollen granule at the contact with the planar end face of the plunger. After the addition of a 0.02—0.03-mL portion of a solvent with a microsyringe onto the sample, the cell was closed, and the curve of a change in the sample size was automatically recorded at room temperature. Under the experimental conditions (up to complete swelling of the sample), the drop volume of the solvent changed only slightly. Toluene, ethanol, chlorobenzene (high purity grade, for chromatography), and diethyl ether (analytical grade) were used as solvents. The changes in the granule diameter were measured with an accuracy of ±0.5 μm. Once the granule diameter ceased to increase in the solvent, *i.e.*, when the equilibrium swollen state was established, the cell containing the sample was opened, and the excess solvent outside the sample was removed with a filtration paper, the monitoring of the changes in the granule size being continued but under the conditions of evaporation (desorption) of the solvent. In some cases, to decrease the evaporation rate, the measurements were carried out in a closed cell containing the sample. To accelerate evaporation, air was purged through the cell (~10 L min^{-1}, 20 °C). The granule deformation during desorption was studied for polymers swollen in organic solvents or in bidistilled water. Since the cross-linked polystyrenes are hydrophobic, the samples preswollen in ethanol were washed on a column with the porous bottom with a large amount of water (10 L per cubic centimeter of granules for 24 h) for the purpose of introducing water.

The bulk deformation e_{sw} of a spherical sample upon absorption or desorption of an organic solvent was calculated by the equation

$$e_{sw} = (V_{sw} - V)/V = [(D_{sw}/D)^3 - 1] \cdot 100,$$

where D and V are the diameter and the volume, respectively, of the dry granule and D_{sw} and V_{sw} are the diameter and the volume of the granule in the course of swelling or drying.

The relative bulk deformation γ of a spherical sample upon desorption of an organic solvent was calculated by the equation

$$\gamma = (V_{sw} - V)/((V_{sw})_{max} - V) = e_{sw}/(e_{sw})_{max},$$

where $(V_{sw})_{max}$ and $(e_{sw})_{max}$ are the maximum volume and deformation, respectively, of the swollen granule.

The accuracy of the determination of e_{sw} was 2% (rel.) for small deformations (for example, 20±0.4%) and 0.8% for large deformations (for example, 200±1.5%). For ten different granules of the same polymer, the deviation from the average for the reproduction of experimental data was at most 10%.

The degree of swelling Q was calculated from the results of prolonged swelling (2—3 days) of a layer of granules under a solvent in a cylinder. For the equilibrium volume of swollen granules $V_{sw,\infty}$, the degree of swelling $Q = V_{sw,\infty}/V$.

The swelling time was determined from the plots of e_{sw} *vs.* t based on the moment of the achievement of the maximum deformation of swelling.

The changes in the size of individual granules during swelling, the position of the solvent front (r/R, where r is the distance from the center of the granule with the radius R to the optical boundary of the front) and the optical effects caused by solvent desorption were observed (and recorded on a video camera) using an optical microscope with a 90-fold magnification in transmitted, reflected, and polarized light.

The moduli of elasticity of the polymers swollen in toluene E_{sw} were determined by uniaxial compression (with an accuracy of 10%) on an UIP-70 instrument.

Studies of the porous structure by low-temperature adsorption of nitrogen and the determination of the true densities of the polymers CPS-100 and CPS-150 (densitometry in helium) were carried out by the Micromeritics Instrument Corp. The above hypercrosslinked polystyrenes have a microporous structure with a pore size of ~3—4 nm and a true density of 1.125 and 1.149 g cm^{-3}, respectively.

The weight swelling a_s of the polymers was determined under static conditions upon adsorption from a liquid phase (toluene or ethanol). Portions of polymers (1—2 cm^3) were kept in toluene or ethanol in a test tube with the porous bottom for 24 h. After removal of the liquid between granules on a centrifuge (15 min, 3000 rpm), the samples were weighted and dried at 100 °C to constant weight (24 h). The adsorption of a solvent was determined as the difference between the weights of the sample before and after drying referred to the weight of the dry sample.

The kinetics of weight loss of swollen samples during desorption of toluene, ethanol, or water was recorded on a Q-1500 (MOM, Hungary) derivatograph at 22±2 °C. After removal of the solvent from the surface of the swollen granules, a weighed sample of a polymer (50—70 mg) was deposited as a one-granule layer onto a network container with the planar bottom mounted on the plunger of the recording system of the instrument. The weights of samples were determined in a weak air flow (~50 mL min^{-1}) in the cell. The weights of the starting (dry) samples were determined after additional drying at 100 °C for 24 h.

The porous structure of hypercrosslinked polystyrenes was studied by dynamic desorption porometry.[18,19]

Results and Discussion

Swelling kinetics. *Gel nonporous styrene—divinylbenzene copolymers* are single-phase materials. They are inert to ethanol but readily undergo swelling in toluene (see Table 1). Investigations of the swelling kinetics of nonporous copolymers in thermodynamically "good" solvents (*i.e.*, in solvents, in which polymer—solvent contacts are energetically more favorable than polymer—polymer and solvent—solvent contacts), the volume of spherical samples increases primarily linearly with time (Fig. 1). As the degree of cross-linking of copolymers increases with increasing amount of divinylbenzene the degree of swelling decreases and the rigidity of a polymer network (measured for the maximum swollen granules) increases. In this case, the modulus of elasticity E_{sw} increases most sharply (from 1 to 12 MPa) in going from the copolymer SD2.7 to SD5.3 (see Table 1) with a simultaneous manifold increase in the swelling time (see Table 1). This is attributed to the fact that an increase in the rigidity of a

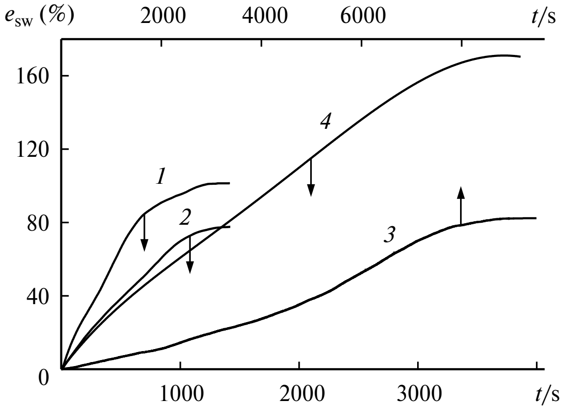

Fig. 1. Swelling kinetics of gel nonporous cross-linked polystyrenes SD1.4 (*1*), SD2.7 (*2*), SD5.3 (*3*), and the polymer CPS-25 (*4*) in toluene.

polymer matrix (increase in the degree of cross-linking) leads to a decrease in the mobility of the chains of the polymer network, which limits the rate of swelling of the network.

The copolymer SD15T, though being prepared in the presence of a porogen (toluene), does not have a pronounced porosity and belongs to densely cross-linked gel polymers (see Table 1). Swelling of a sample of SD15T in toluene to the equilibrium state is completed in >5000 s; however, this time is substantially shorter than the swelling time (8700 s) of the more lightly cross-linked copolymer SD5.3, which was prepared in the absence of toluene. Apparently, the synthesis of the polymer SD15T in the presence of toluene leads to a decrease in the degree of entanglement of the polymer chains. As a result, the swelling of this polymer in toluene increases from 1.4 to 1.6 compared to that of the analogous polymer SD15 synthesized in the absence of porogens, and the modulus of elasticity of the swollen sample decreases by a factor of 4. Presumably, the polymer SD15T tends to have a porous structure. Actually, a pronounced porosity of styrene copolymers is observed[20] in the presence of either divinylbenzene in an amount of >15% or toluene in an amount of >60%.

Macroporous polymers, such as the styrene copolymer SD15H and poly(divinylbenzenes) DH and DT, which were synthesized in the presence of hexane and toluene, respectively, substantially differ from gel copolymers (Fig. 2). The degrees of swelling for macroporous polymers are very low, and the time dependences of deformations are nonlinear and nearly exponential. In spite of a substantially higher percentage of cross-linking divinylbenzene fragments, swelling of these porous polymers in toluene occurs much more rapidly than that of the nonporous gel-type lightly cross-linked copolymer SD1.4 (see Table 1). In the presence of the same percentage (15%) of divinylbenzene, the swelling rate of macroporous SD15H in toluene is also much higher than that of the gel polymer SD15T, though the equilibrium degree of swelling being somewhat lower. It should be noted that the polymer SD15H adsorbs up to 0.63 mL g^{-1} of ethanol, the volume remaining virtually unchanged, which is indicative of pronounced macroporosity of the polymer. Actually, the apparent density of the polymer SD15H (see Table 1) is at most 0.68 g cm^{-3}.

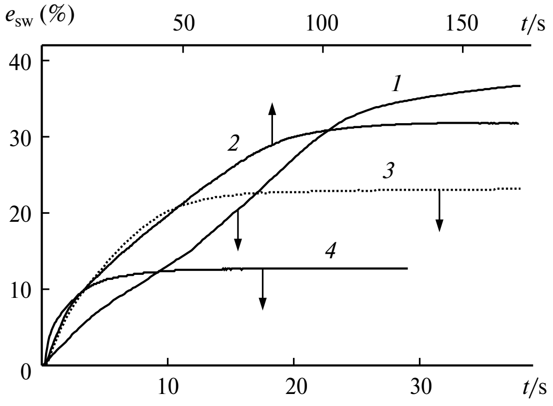

Fig. 2. Swelling kinetics of porous cross-linked polymers, *viz.*, the styrene copolymer SD15H (*1*) and poly(divinylbenzenes) DT (*2*), XAD-4 (*3*), and DH (*4*), in toluene.

The swelling rate of macroporous poly(divinylbenzene) DH in toluene is 10 times higher than that of porous poly(divinylbenzene) DT, in spite of the same chemical composition and a developed porous system of both networks (S_{in} = 580 and 450 m^2 g^{-1}, respectively). The increase in the volume of the polymer DT upon swelling is twice as large as that of DH (see Fig. 2).

The commercial sorbent XAD-4 also belongs to highly porous poly(divinylbenzenes) and was synthesized in the presence of a porogen (most likely, a mixture of solvating and nonsolvating solvents). That is why its properties are somewhat different from those of the polymer DH (see Table 1). Swelling of the polymer XAD-4 in toluene proceeds, though with a slight increase in the volume (23%), very rapidly, and the curve of swelling of this polymer has a pronounced exponential character (see Fig. 2). The monitoring of swelling with an optical microscope showed that the solvent front reaches the center of a spherical sample of XAD-4 in a few seconds. In our opinion, a high rate of migration of the adsorbate in the polymer XAD-4 is attributed to a highly developed system of macro- and mesopores (up to the sizes close to the sizes of micropores[21]). This is confirmed by the very low density (0.52 g cm^{-3}) and the high specific surface area (900 m^2 g^{-1}) of the polymer (see Table 1).

In our opinion, the exponential character of the swelling kinetics of the polymer XAD-4 and other macroporous copolymers is a consequence of very rapid wetting with toluene (through a developed system of macropores) of the total bulk of granules and much slower swelling of the highly cross-linked polymeric phase of the macropore walls of the granules. It should be emphasized once again that the volume of all macroporous copolymers (except for DT and XAD-4) increases only in thermodynamically "good" solvents, the increase being much smaller than that observed for gel structures.

Hypercrosslinked polystyrenes differ from the above-considered classical polymer networks in the parameters of the swelling process (see Table 1). Thus, hypercrosslinked polystyrenes can undergo swelling not only in toluene but also in ethanol and are characterized by higher degrees and rates of swelling. It should be noted that the polymer CPS-25 (which was synthesized with the use of 0.2 mol of a bifunctional cross-linking agent per mole of monomer units of polystyrene) can only be formally assigned to hypercrosslinked copolymers because this rather lightly cross-linked network polystyrene is still similar in properties to gel-type polymers. It should be noted that the degree and rate of swelling of the polymer CPS-25 in toluene are ~2 and 1.3 times higher that the corresponding parameters of the copolymer SD15T containing an even slightly smaller number of cross-linking sites. This is due to a decrease in the degree of mutual entanglement of macrochains of CPS-25 in the case of the synthesis of the latter by cross-linking the lightly cross-linked styrene copolymer highly swollen in an appropriate solvent.

The use of large amounts of a bifunctional agent for cross-linking of polystyrene chains in samples from CPS-43 to CPS-200 leads to the formation of hypercrosslinked polystyrenes characterized by a special structure of the polymer matrix and an abnormally large free volume. The latter have unique sorption and mechanical properties and are sharply different in swelling kinetics from macroporous copolymers and macroporous poly(divinylbenzenes) (see Table 1). Hypercrosslinked polystyrenes have highly cross-linked but expanded loose micro- and mesoporous polymer networks. Unlike macroporous polymers, the latter polymers are single-phase in the sense that their structure cannot be divided into the pore phase and the polymer phase. The glass transition temperature or region, which are clearly observed for nonporous and macroporous structures, are not typical of hypercrosslinked polystyrenes.

For hypercrosslinked copolymers with a degree of cross-linking >66%, the volume of granules increases during adsorption of toluene and ethanol very rapidly, and the granule volume increases by a factor of almost 3 (see Table 1). It should be noted that the deformation rate of swelling sharply increases with increasing degree of cross-linking of polymers (Fig. 3), whereas the swelling time decreases: in toluene, from 3700 to 40 s for CPS-25 and CPS-200, respectively; in ethanol, from 2300 to 80 s for CPS-43 and CPS-200, respectively. The character of kinetic curves substantially changes from an almost linear deformation curve extended on the time scale for gel cross-linked polystyrene CPS-25 and other gel networks (see Fig. 1) to sigmoidal swelling curves for hypercrosslinked polystyrenes, which are clearly observed in a short time range (see Fig. 3). Studies of swelling of hypercrosslinked copolymers by optical microscopy showed that deformations of swelling are developed rather slowly in the initial step of the process, until the solvent front reaches the center of a spherical sample (Fig. 4). In the second step, after complete wetting of the total bulk of samples of hypercrosslinked copolymers, the rate of the deformation process sharply increases. Taking into account a high degree of cross-linking of hypercrosslinked copolymers (up to 200%), the fact of a threefold increase in their volume can be attributed only to a cooperative conformational rearrangement of all elements of the three-dimensional network of samples. This rearrangement becomes possible only after wetting of the total bulk of granules by the solvent. By contrast, substantial bulk deformations in networks containing rather long chain fragments between the cross-linking sites, like in gel copolymers and even in the polymer CPS-25, can start immediately in plastified and solvent-solvated surface areas of granules regardless of the stationary granule core, which is still unwetted by toluene.

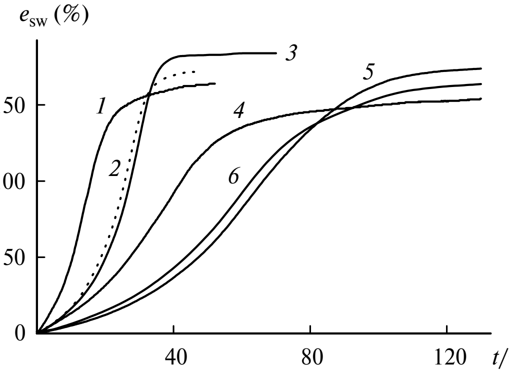

Fig. 3. Swelling kinetics in toluene (*1*—*3*) and ethanol (*4*—*6*) of hypercrosslinked polystyrenes CPS-200 (*1*, *4*), CPS-100 (*2*, *5*), and CPS-66 (*3*, *6*).

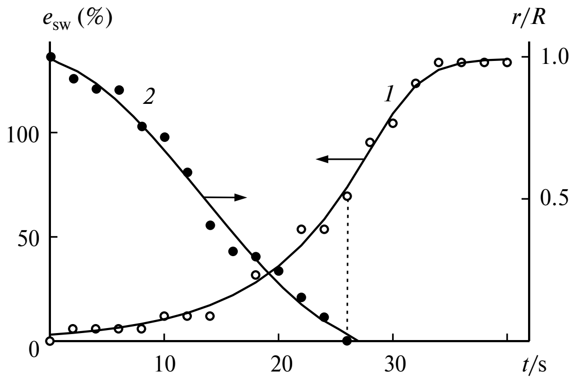

Fig. 4. Swelling kinetics (*1*) and migration of the optical boundary of the solvent (toluene) front (*2*) in a spherical sample of the polymer CPS-100.

When considering the behavior of hypercrosslinked networks, it should be emphasized that, unlike classical gel and macroporous polymers, hypercrosslinked polystyrenes undergo swelling in media, which do not dissolve polystyrene (for example, in ethanol), almost as extensively (more than a twofold increase in the volume) as in thermodynamically good solvents (toluene). It can be noted that deformations of granules in ethanol proceed much more slowly than in toluene. Apparently, toluene accelerates conformational rearrangements because of better solvation of polymer chains.

Second, it should be noted that an increase in the degree of cross-linking of hypercrosslinked copolymers accelerates the development of swelling deformations, the maximum degree of swelling being only slightly lower. An increase in the degree of cross-linking also does not lead to a sharp increase in the structural rigidity. Thus,

E_{sw} increases from 27 MPa for a polymer with a degree of cross-linking of 100% to only 42 MPa for a polymer cross-linked by 200%. In addition, it can be noted that there is a general correlation between the equilibrium swelling of polymers in toluene and the rigidity of their structures (modulus of elasticity) in the swollen state. This correlation is observed both in a series of samples of hypercrosslinked copolymers and, to even a larger degree, in comparing the structurally flexible and highgly swelling hypercrosslinked copolymers characterized by small moduli of elasticity with rigid XAD-4-, DT-, and DH-type polystyrene networks (see Table 1).

Therefore, the unique sorption properties, as well as the kinetic characteristics of swelling of hypercrosslinked copolymers, are attributed to their microporosity, substantial structural mobility of a loose polymer network, and large internal stresses, which relax upon sorption and swelling. Internal stresses occur upon removal of the solvent from a hypercrosslinked network formed in the unstressed state in thermodynamically good solvents. The stressed state of dry hypercrosslinked polymers is a powerful driving force of swelling,[22,23] which is responsible for the ability of swelling in all liquids and a high rate of bulk deformations. The presence of internal stresses in dry granules and their relaxation upon swelling are clearly seen in interference images of granules under a polarized light microscope. The largest stresses are typical of samples characterized by the maximum degree of cross-linking. The swelling rate and the apparent inner surface area increase in the same series. These characteristic features are undoubtedly responsible for considerable advantages of hypercrosslinked polystyrenes serving as fast and efficient sorbents.

Internal stresses would be present in a certain degree in samples of DT and XAD-4, whose networks were synthesized in the presence of a thermodynamically good solvent and, hence, can undergo swelling in ethanol.

To summarize the data on swelling deformations of individual granules of various polystyrene-type copolymers, it should be noted that there are principal differences in the swelling kinetics of gel-type, macroporous, and hypercrosslinked structures. Swelling of gel copolymers in thermodynamically good solvents is virtually linear in time, is accompanied by slow diffusion of the solvent to the center of granules, and is characterized by large final deformations. In macroporous structures, very rapid wetting of the total bulk of granules with the simultaneous fast but insignificant increase in the volume of the granules is followed by slow (and insignificant) swelling of a highly cross-linked polymer phase of the pore walls in thermodynamically good solvents. Hypercrosslinked networks are characterized by a very fast and considerable increase in the volume of granules in all liquid media, the rate of the process being sharply increased after wetting of the total bulk of microporous granules by a solvent.

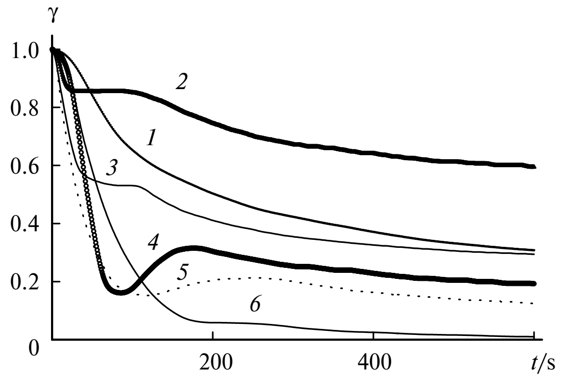

Fig. 5. Deformation of gel (*1*) and porous cross-linked polymers (*2*—*6*) during desorption of toluene: SD-2.7 (*1*), DH (*2*), SD15H (*3*), XAD-4 (*4*), DT (*5*), and CPS-200 (*6*).

Deformation of polymers during solvent desorption. The procedure, which we have developed for precise measurements of fast changes in the granule size, allowed us to study in detail not only swelling of polymers but also the characteristics of the volume changes during solvent desorption[24] (Fig. 5). We observed for the first time the anomalous character of changes in the volume during drying (deswelling) for porous polymers. Thus, the time dependence of deformations shows a step or even a pronounced extremum rather than is characterized by a smooth decrease in the volume of the swollen spherical sample (see Fig. 5). This effect is observed for all macroporous polymers DH, DT, and SD15H, the polymer XAD-4, and (to a much lesser extent) for the microporous hypercrosslinked networks CPS-150 and CPS-200, but is completely absent in the case of gel nonporous styrene copolymers.

The anomalous character of the deformation process in the case of desorption of solvents from the polymer XAD-4 (Figs 5 and 6) is most pronounced. Thus, the

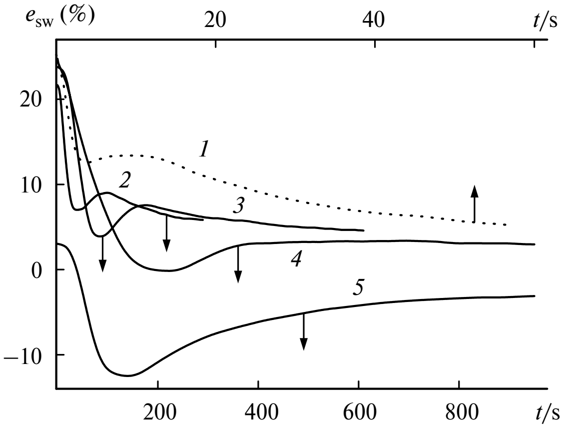

Fig. 6. Deformation of macroporous poly(divinylbenzene) XAD-4 during desorption of solvents of different nature: diethyl ether (*1*), ethanol (*2*), toluene (*3*), chlorobenzene (*4*), and water (*5*).

volume of a swollen granule of XAD-4 regularly decreases but, at a particular instant of time (for example, after 100 s for toluene), the volume substantially increases followed by a slow decrease to the final minimum volume of the dry granule. An anomalous increase in the volume of the polymer XAD-4 was observed upon desorption of organic solvents of various nature (see Fig. 6). The intermediate increase in deformations for diethyl ether, ethanol, chlorobenzene, and toluene was 0.9, 1.5, 3.5, and 3.5%, respectively.

Since the anomalous increase in the volume caused by desorption is not associated with irreversible structural rearrangements, this effect is well reproduced in cyclic swelling and drying (Fig. 7).

This effect persists for nonspherical samples (hemispherical samples of XAD-4, samples of quarter-spherical shape, and samples of irregular shape were studied). This effect also does not disappear with changes in the desorption conditions (Fig. 8), in particular, in the case of a substantial increase in the drying rate. Therefore, the observed phenomenon reflects the thermodynamically equilibrium rather than the kinetic effect.

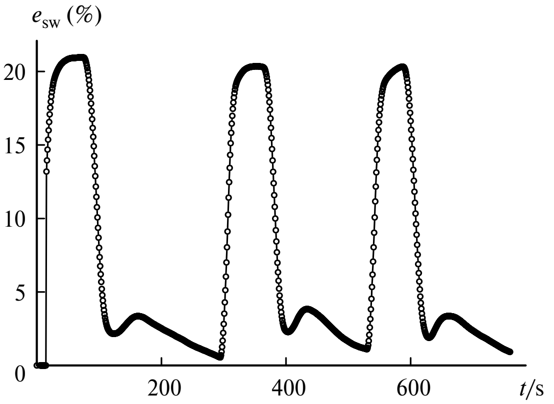

Fig. 7. Deformation of macroporous poly(divinylbenzene) XAD-4 during cyclic swelling and desorption of ethanol.

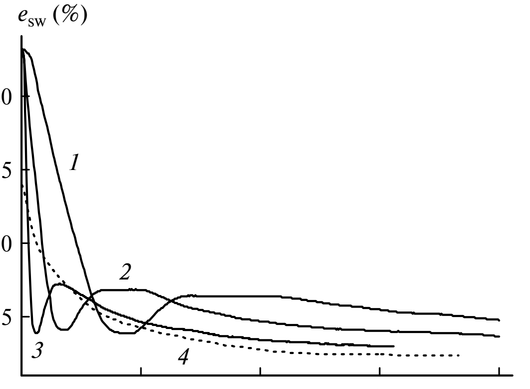

Fig. 8. Influence of the conditions of desorption of toluene on deformation of the polymer XAD-4: *1*, the sample is isolated from an air flow; *2*, an open cell, weak convection air flow; *3*, purging of air through a cell (~10 L min^{-1}, 20 °C); *4*, an open cell, a sample after sorption of toluene vapor (in a closed cell of an instrument for 740 s).

Most probably, the solvent is initially evaporated from macropores and then from successively smaller pores. It is reasonable to suggest that the residual liquid in small pores forms concave meniscuses at the exits of pores and capillaries and exists under reduced pressure, resulting in the well-known effect of capillary contraction.[25] In this case, polymer networks with a porous structure analogous to that of the polymer XAD-4 have elastic local deformations (Fig. 9) in a microcapillary region, which are manifested in an excessive decrease in the volume of granules. As the liquid is released from microcapillaries, the volume of the sample increases as a result of relaxation of these elastic strains. Then the volume of granules slowly decreases due to desorption of the solvent from the polymer phase of the pore walls. It is reasonable that the kinetic curves of desorption, *i.e.*, the weight loss curves upon evaporation of toluene or other solvents, have no extreme regions (Fig. 10).

After storage of a sample of dry XAD-4 in toluene vapor, the sample adsorbs a substantial amount of toluene and increases in size. However, we did not observe an anomalous increase in the volume upon desorption of toluene from this sample. Apparently, vapor sorption of toluene did not lead to condensation of the liquid in

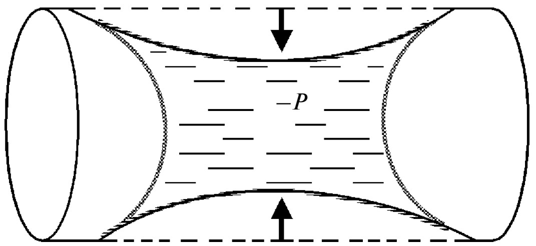

Fig. 9. Elastic deformation of the capillary walls of porous polymers during desorption of an liquid.

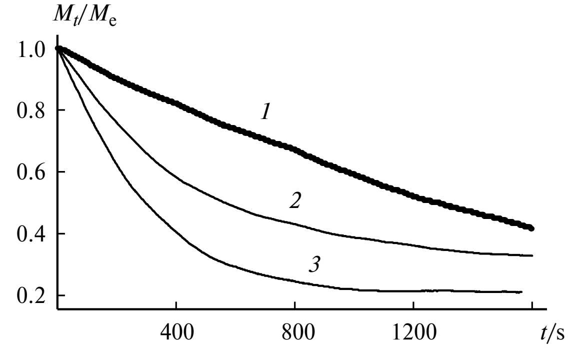

Fig. 10. Kinetics of desorption of water (*1*), toluene (*2*), and ethanol (*3*) from the polymer XAD-4; M_t and M_e are the amounts of the sorbate at the instant of time t and in the sorption equilibrium state, respectively.

capillaries of the material and, consequently, could not lead to capillary contraction. Actually, the amplitude of bulk deformations e_{sw} of granules swollen in the vapor was only 50—60% of the bulk deformations upon drying of the granules subjected to swelling in liquid toluene.

The most pronounced anomalous bulk deformations were observed during desorption of water from the polymer XAD-4 (see Fig. 6). This porous polymer can retain up to 1 g g^{-1} of water without substantial swelling ($Q = 1.03$, the increase in the volume is at most 2—4%). The polymer phase is not solvated and plastified by water, and the latter only fills the pore space of this poly(divinylbenzene) sample. The modulus of elasticity of the dry sample (450 MPa) is very similar to that of the sample filled with water (400 MPa). However, upon removal of water, the volume of granules not only decreases by 2—4% (to the dry volume) but also goes to a negative deformation region, thus additionally decreasing by 12% with respect to the equilibrium volume of the dry granules. Only in the next step of drying, after the step of forced contraction due to capillary contraction, the volume of granules slowly increases and restores the equilibrium dry volume.

The deformability of the XAD-4 polymer network is much more influenced by ethanol or toluene. Swelling of XAD-4 in these solvents leads to an increase in the volume by 22%, *i.e.*, to a much larger increase compared to that in water (see Table 1). Due to plastification by organic solvents, the modulus of elasticity of swollen samples is substantially lower (by a factor of 2). The amplitude of the anomaly in the case of water desorption is ~12% of the volume of granules, whereas the amplitude of anomaly in the case of evaporation of toluene or methanol is as small as 3.5%. The force developed by the capillary contraction for the achievement of such deformations can be estimated at 400 and 60 atm, respectively. It should be noted that the surface tension at the liquid—vapor interface for water is substantially larger than that for these organic solvents.

The observation of the drying process of swollen granules and attendant deformations by optical microscopy revealed unusual optical effects, which are coincident with the period of an anomalous increase in the volume upon drying. The polymer XAD-4 swollen in ethanol is virtually transparent in normal and polarized light. The partial replacement of ethanol in pores of granules by air during solvent evaporation gives rise to pronounced scattering heterogeneous regions. This instant of time, when some pores are filled by the liquid, while other pores are filled with air, corresponds to a minimum in the volume *vs.* time curve. Then the liquid disappears from pores, and the volume of granules again slightly increases once the deformed pore walls are restored. This also leads to an increase in the scattering ability of the heterogeneous material and granules with expanded pores become nontransparent. This instant of time corresponds to a maximum in the time dependences of deformation. Finally, the material undergoes further shrinkage to the equilibrium denser state as the adsorbed solvent solvating the polymer phase is lost. The expanded pores decrease in size and the material again becomes more transparent.

Undoubtedly, the specific structure of pores and particular flexibility of the framework favor the a more pronounced anomaly of the deformation process during desorption of solvents from the sorbent XAD-4 compared to other sorbents. An anomalous extremum in the time dependences of deformation degenerates into a step for the macroporous sorbents SD15H and DH (see Fig. 5). Apparently, the structure in the lighter cross-linked copolymer SD15H is more flexible than that in poly(divinylbenzene) XAD-4 (modulus of elasticity of swollen SD15H is 2.5 times smaller). Hence, solvent desorption cannot give rise to temporary elastic deformations, which can cause a further increase in the volume. In addition, the total volume of micro- and mesopores in the polymer SD15H is small taking into account the insignificant absorption of ethanol and the small specific surface area ($S_{in} = 70$ m^2 g^{-1}) of the material. In spite of the well-developed system of pores ($S_{in} = 580$ m^2 g^{-1}), the polymer DH apparently cannot undergo considerable elastic deformations upon capillary contraction, because its matrix is too rigid, and its modulus of elasticity is twice as large as that of the polymer XAD-4 (see Table 1).

For hypercrosslinked polystyrenes swollen in different organic solvents, an anomalous change in the volume caused by desorption is also much less pronounced than that for the polymer XAD-4, and is noticeable only for samples, which are characterized by the degree of cross-linking larger than 100% and are swollen in diethyl ether or water (Fig. 11). Apparently, hypercrosslinked polystyrenes are much more homogeneous in the sense that they do not contain pronounced pores with dense walls, in which microdrops of liquids with a concave meniscus could be formed. In addition, hypercrosslinked polysty-

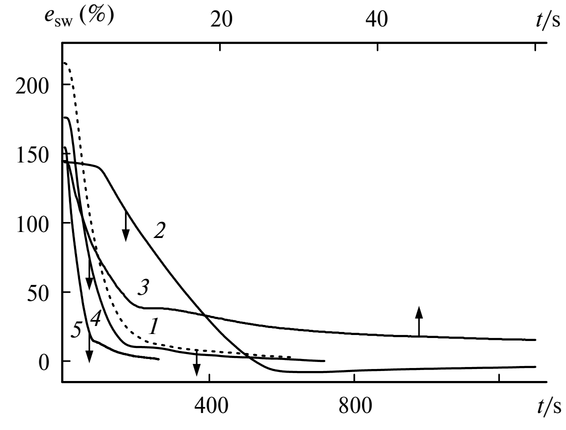

Fig. 11. Deformation of hypercrosslinked polystyrenes CPS-100 (*1*) and CPS-200 (*2—5*) in the course of desorption of water (*2*), diethyl ether (*3*), toluene (*1*, *4*), and ethanol (*5*).

renes are characterized by very large structural mobility of the network (their moduli of elasticity are four times smaller than that of XAD-4), which also can decrease the probability of the appearance of elastic local deformations in the case of capillary contraction. Nevertheless, evaporation of water from hypercrosslinked polystyrene CPS-200 is accompanied by an excessive decrease in its volume by 8% compared to the dry granules (see Fig. 11). Further final drying and relaxation of negative deformations, which result in the recovery of the "dry" size of granules, proceed rather slowly (over a period longer than 2000 s).

Presumably, the steps in the volume change curves measured in the course of drying of all macroporous and hypercrosslinked polymers are attributed to the same changes in the thermodynamic parameters, which can be associated with capillary contraction. It should be borne in mind that the total changes in the volume of granules of hypercrosslinked polymers during drying of any solvent are very large and are estimated at hundreds of percentage, *i.e.*, are an order of magnitude larger than that for macroporous polymers, including the polymer XAD-4.

Dynamic desorption porometry. The automated monitoring of the weight of swollen polymers in the course of solvent evaporation provides the basis for dynamic desorption porometry.[18,19] We applied this method to studies of hypercrosslinked polystyrene CPS-100 (Fig. 12) swollen in different solvents. Regardless of the polarity of adsorbates (except for water), the starting state of the polymer in the swollen state includes an approximately equal (abnormally large) total volume of adsorbates. Studies by dynamic desorption porometry demonstrated that this volume is ~2.8 cm^3 per gram for CPS-100, which is substantially larger than the volume of pores in the dry polymer (~0.43 cm^3 g^{-1}) and is indicative of a large swelling of granules. In studies by dynamic desorption porometry, the curves of the solvent evaporation rate (under strictly controlled conditions) are converted into the isotherms of solvent desorption (see Fig. 12). Dynamic desorption porometry showed that ~0.075 cm^3 g^{-1} of the liquid remained in samples after desorption of hexane or benzene at room temperature. This "irreversible" adsorption is indicative of strong interactions between the residual solvents and the hypercrosslinked polymer matrix of the sample (or of a substantial decrease in the diffusion rate due to shrinkage of the porous structure and trapping of sorbate molecules in very small cavities (at most 1—3 nm in the dry polymer). The desorption isotherm of polar methanol is indicative of a weaker interaction between methanol and the material of the sample.

Cumulative distributions with respect to the potentials of adsorption $RT\ln(p_0/p)$ (liquid—solid bond energies according to Rebinder) calculated from the desorption isotherms are shown in Fig. 13. The series of the curves in Fig. 13 from the left to the right correlates with the series of the dielectric permeabilities (*i.e.*, the polarities) of the adsorbates: water (81), methanol (33.7), benzene (2.23), and hexane (1.89). As can be seen from Fig. 13, methanol desorption occurs at substantially lower potentials of adsorption (~3 times lower) compared to hexane desorption. For example, approximately half of the volume of methanol is desorbed at the bond energy with the sorbent <0.3 kJ mol^{-1}, whereas the corresponding energy for hexane is ~1 kJ mol^{-1}. Apparently, the difference between these values (~0.7 kJ mol^{-1}) may characterize the difference in the energy of solvation of polystyrene by these liquids. This value agrees with the difference between the integral heats of wetting and swelling of hypercrosslinked polystyrene by methanol and hexane measured earlier.[15]

Water desorption radically differs from desorption of other adsorbates. The initial volume of "adsorbed" water in CPS-100 is 0.98 cm^3 g^{-1}, which is three times smaller than the retained volumes of organic solvents but is twice as large as the volume of pores of the dry sample. An approximately the same volume (0.9 cm^3 g^{-1}) of nitrogen is condensed in this polymer at liquid nitrogen temperature. Evidently, these volumes correspond to equilibrium swelling of the material in water and in liquid

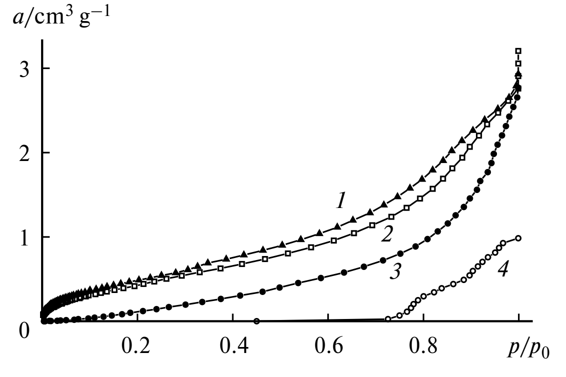

Fig. 12. Isotherms of desorption from the polymer CPS-100: hexane (*1*), benzene (*2*), methanol (*3*), and water (*4*).

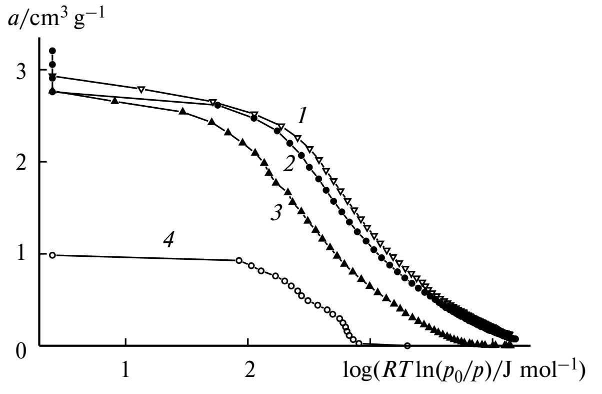

Fig. 13. Volume distributions for adsorbates with respect to the potentials of adsorption for the polymer CPS-100: hexane (*1*), benzene (*2*), methanol (*3*), and water (*4*).

nitrogen. This has been discussed in the earlier studies.[28] Water in small hydrophobic cavities of hypercrosslinked polystyrene should substantially differ in the structure and properties from bulk water. It should be noted that a nonmonotonic curve of water evaporation may be indicative of a bimodal size distribution of small pores in this sample. However, the question of whether the stepwise character of water evaporation is associated with the extreme character of deformations of porous materials during desorption of water and other solvents requires further elucidation. Among many methods of investigation of porous structures of hypercrosslinked polystyrenes,[26] only positronium annihilation[27] also provided evidence for the possible polymodal distribution of small pores.

To summarize, in the present study we developed a new automated method for monitoring fast changes in the size of spherical samples of polymers during their contact with a solvent and drying. The method provides quantitative characteristics of the kinetics of deformation in the course of swelling of gel-type, macroporous, and hypercrosslinked styrene polymers and desorption of solvents from polymers.

The principal differences were revealed in the degree, rate, and kinetic characteristics of swelling of polystyrene networks of three main types, *viz.*, gel-type, macroporous, and hypercrosslinked. These differences are associated with the differences in the driving force of swelling, the diffusion rate of solvents into samples, and the rate of conformational rearrangements of structural elements of the networks.

An anomaly of the deformation process of porous materials during desorption was found. This anomaly is manifested in a temporary sharp increase in the volume (which gradually decreases) of samples during desorption of organic solvents and is most pronounced in the porous polymer Amberlite XAD-4. During drying of the polymer XAD-4 filled with water, an anomalous contraction followed by relaxation of negative bulk deformations to the equilibrium volume of the dry sample were observed.

The nonmonotonic character of water desorption from hypercrosslinked polystyrene observed by dynamic desorption porometry may be indicative of a bimodal distribution of micropores in the samples under study.

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