Mechanical Behavior and Structure of Single Beads of Homogeneous and Macroporous Styrene–Divinylbenzene Copolymers

P. P. WIECZOREK,* M. ILAVSKÝ, B. N. KOLARZ,* and K. DUŠEK,

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Synopsis

The stress–strain and ultimate behavior in compression of homogeneous and macroporous beads of styrene–divinylbenzene copolymers has been investigated in the dry state or in equilibrium with toluene, acetone, methanol, and water. The penetration modulus A indicates sensitively the transition from the glassy into the rubbery state induced by an increase in temperature or swelling. For macroporous copolymers, A of the glassy polymers is mainly determined by the porosity P, while in the rubbery region it primarily depends on the matrix structure (degree of crosslinking and concentration and composition of the diluent). The high value of the slope s of the A vs. P dependence ($s \approx -3$) for macroporous copolymers is evidence of the complex deformation mechanism (buckling of pore walls). The relative compression at break, $\epsilon_b = 0.3$–0.4, is independent of the composition, and the compressive strength is roughly proportional to the penetration modulus.

INTRODUCTION

Copolymers of styrene (S) and divinylbenzene (DVB) prepared by suspension copolymerization in the presence of inert additives are a sought-for sorption material suited for many applications because of the variability of their porous structure and the network density of the matrix. Relationships between the way of preparation, structure, and properties of these materials have been dealt with in many articles.[1–6] Combined equilibrium mechanical and swelling measurements of S-DVB copolymers prepared in the absence of additives (denoted as homogeneous, standard, or gel type) have so far been carried out on samples prepared in bulk, in order to specify their structure and provide basic data for the interpretation of the behavior of macroporous copolymers.[2,7–10]

Recent measurements performed with bead cellulose and copolymers of glycidyl methacrylate and ethylene dimethacrylate demonstrated the possibility of determining the penetration modulus and strength by compression measurements on the individual beads.[11–13] These measurements can be utilized not only in structural studies and in the characterization of the distribution of structural parameters of an assembly of beads; they are also of great importance in applications because they determine the deformability of beads and hence the resistance of the sorbent bed in column separations. The bead strength determines the durability of the packing.

In this study, the techniques just described have been used in the characterization of a number of homogeneous and macroporous S-DVB copolymers with

varying DVB concentration and concentration and composition of the diluent. It is known that permanent porosity is due to phase separation with the assistance of the specificity of the chain crosslinking copolymerization (prevailing cyclization and occurrence of compact, internally crosslinked particles[2,3,14,15]). Transient macroporosity induced by decreasing solvent power of the swelling agent and caused either by a temperature change or solvent exchange may also appear in the copolymers.[16–20] The transition of the system into the glassy state during removal of the swelling agent seems to be the main cause why the induced porous structure and sometimes also the chemically fixed porosity remain preserved. The properties of such a series of bead copolymers, in which deswelling was reached by a gradual exchange of the solvents, have been examined also in this report as a continuation of earlier studies.[17,18,20]

EXPERIMENTAL

Synthesis of Copolymers

Styrene (Z. CH. Oswiecim, Poland) was freed from the inhibitor by shaking with 20% aq. NaOH, washing, and drying, followed by distillation under reduced pressure in a stream of argon. Divinylbenzene (Merck, FRG) was freed from the inhibitor and distilled similarly; the GLC analysis gave the following result: 12.7% p-DVB, 38.1% m-DVB, 14.3% p-ethylvinylbenzene, and 34.0% of m-ethylbenzene. Reagent-grade heptane and toluene (POCh, Gliwice, Poland) were used as diluents.

The S-DVB copolymers were obtained by the suspension polymerization method. Dibenzoyl peroxide (POCh, Gliwice, Poland) was used as the initiator (1 wt % in relation to the monomers). The suspension was stabilized by using 0.1 wt % aqueous poly(vinyl alcohol) (Rohm and Haas Co.). The polymerization was carried out at 343–368 K in a 2 dm³ reactor equipped with a propeller-type stirrer with two blades at different levels. After polymerization the copolymers were washed with hot water and methanol and then extracted with benzene. After the extraction, the copolymers were transferred into a chromatograph column and washed with the following series of solvents: toluene, acetone, methanol, and water, according to the method described earlier.[17,18]

Four series of copolymers were prepared (Table I). In series I, the homogeneous gels were coded as follows: S/50 means that the copolymer contains 50 wt % DVB in the monomer mixture. Series II–IV include the solvent-modified copolymers obtained in the presence of a mixture of toluene (T) and heptane (H). For example, the symbol HT 19 0.3/50 means that the volume ratio of heptane to toluene is 1:9, 0.3 is the initial volume fraction of the monomer (Styrene + DVB), and 50 is the wt % of DVB in the monomer.

Measurements

Porosity

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method by using an apparatus described earlier[19] and for copolymers obtained by drying of samples swollen in toluene at 420 K. Porosity P was

TABLE I
Composition and Swelling of Styrene–Divinylbenzene Copolymers[a]

Series	Sample	Sample no.	d_0, 10^{-3} kg/m^3	P	v_2			
					TOL	ACET	MET	H$_2$O
I	S/10	1	1.05	0	0.598	0.758	0.847	0.885
	S/20	2	1.05	0	0.758	0.813	0.840	0.901
	S/30	3	1.05	0	0.806	0.855	0.862	0.909
	S/40	4	1.05	0	0.820	0.862	0.870	0.909
	S/50	5	1.05	0	0.781	0.820	0.877	0.962
II	HT 19 0.5/50	6	0.83	0.210	0.602	0.641	0.641	0.820
	HT 17 0.5/50	7	0.85	0.190	0.562	0.571	0.617	0.800
	HT 15 0.5/50	8	0.83	0.210	0.581	0.585	0.575	
	HT 13 0.5/50	9	0.77	0.267	0.714	0.709	0.752	
	HT 11 0.5/50	10	0.76	0.276	0.746	0.735	0.762	
III	HT 19 0.75/50	11	1.01	0.038	0.746	0.756	0.746	0.893
	HT 19 0.5/50	12	0.83	0.210	0.602	0.641	0.641	0.820
	HT 19 0.4/50	13	0.76	0.276	0.495	0.508	0.595	0.781
	HT 19 0.3/50	14	0.77	0.267	0.403	0.442	0.441	0.581
	HT 19 0.2/50	15	0.85	0.190	0.227	0.242	0.242	0.369
IV	HT 19 0.5/50	16	0.83	0.210	0.602	0.641	0.641	0.820
	HT 19 0.5/40	17	0.96	0.086	0.602	0.662	0.676	0.826
	HT 19 0.5/30	18	1.03	0.019	0.559	0.602	0.675	0.840
	HT 19 0.5/20	19	1.04	0.010	0.581	0.667	0.690	0.855
	HT 19 0.5/10	20	1.05		0.575	0.637	0.662	0.855

[a] TOL = Toluene, ACET = acetone, MET = methanol, P = porosity, d_0 = apparent density of copolymer, v_2 = volume fraction of the polymer in the gel phase. Designation of samples S/X means standard (homogeneous) copolymer with X wt. % DVB; HT UV Z/X means a copolymer prepared in the presence of hexane and toluene at the volume ratio U:V, the initial volume fraction of monomer is Z and the monomers contain X wt.% DVB.

calculated as $P = 1 - d_0/d_2$, where d_2 is the density of the homogeneous S-DVB copolymers ($d_2 \approx 1050$ kg/m^3, Table I).

Swelling

Swelling in all solvents was determined by two independent methods:

(a) From the weight swelling ratio W, which was determined by the centrifugation method, the volume swelling ratio B_1 was calculated from a relationship[10] given earlier:

$$B_1 = \frac{d_0}{d_{2,r}} + \frac{(W - 1)d_0}{d_1} \tag{1}$$

where d_1 is the density of the solvent and $d_{2,r}$ is the density of the copolymer in the rubbery state (≈ 1090 kg/m^3).

(b) By measuring the respective diameters D of a swollen and dry bead (dried under reduced pressure at 393 K for two weeks) using an Abbé comparator (Zeiss Jena, accuracy $\pm$ 0.002 mm), the swelling ratio was then $B_2 = (D_1/D_2)^3$. The values of the swelling ratios B_1 and B_2 obtained with both these methods differed only within the experimental error. The volume fraction of copolymer in the swollen gel, v_2, was calculated from their mean, $B = (B_1 + B_2)/2$, by using a relationship[10] given earlier:

$$v_2 = \frac{d_2}{d_{2,r}B} \tag{2}$$

which is fulfilled for isotropic swelling of the network (the bead matrix).

Mechanical Properties

The mechanical and ultimate properties in simple compression of a single bead were determined using an apparatus described in detail earlier.[11,12] Several beads (three to five) of each copolymer were used for measurements in the dry and swollen states at 298 K. Only beads with radii $r \geq 0.25$ mm were employed, since for smaller r the modulus was found to depend markedly on the radius.[11,12] For some copolymers swollen in toluene and water, the measurements were carried out at 298–368 K.

The maximum force that could be measured was 100 N, and the deformation y was determined with an accuracy of ± 0.0005 mm. When the bead was deformed (compressed) by the value of Δy, the force F was recorded after 30 s of relaxation; the compression was raised and the whole procedure was repeated until the sample failed. An example of the measured dependences of $F^{2/3}$ on y is shown in Figure 1. The penetration modulus A was calculated using the equation[11]

$$A = \frac{3(2s)^{2/3}}{16 r^{1/2}} \tag{3}$$

where r is the bead radius and s is the initial slope of the dependence of $F^{2/3}$ on y (Fig. 1). The stress at break, σ_b, was related to the deformed bead surface area:

$$\sigma_b = \frac{F_b}{\pi \, \Delta y_b \, [r - (\Delta y_b/4)]} \tag{4}$$

where F_b is the breaking force and $\Delta y_b = y_b - y_0$ (cf. Fig. 1) is the maximum compression at break.

The relative compression at break, ϵ_b, was calculated using the formula $\epsilon_b = \Delta y_b/2r$.
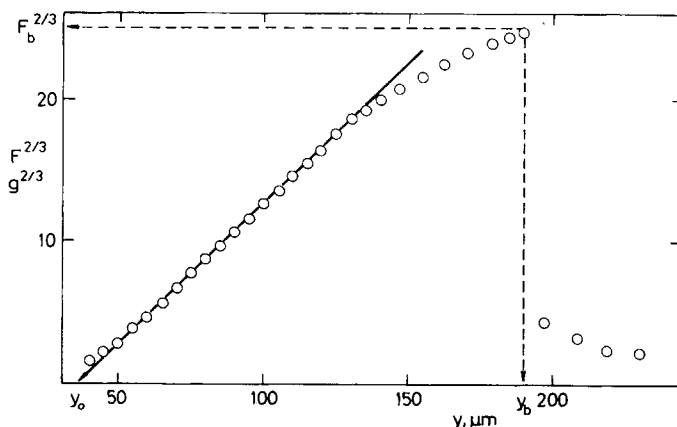

Fig. 1. Example of dependence of force F on compression y for sample 1 in Table I.

RESULTS AND DISCUSSION

Homogeneous Copolymers

The degree of swelling of homogeneous copolymers exhibits the expected dependence on the DVB concentration and the quality of the solvent (Table I, Fig. 2). The nonnegligible degree of swelling in such poor solvents as methanol and water (even linear polystyrene does not virtually swell there) is given by the technique of solvent exchange and requires some comments.

On transition from a good to a poor solvent, microsyneresis connected with the formation of a secondary porous structure may appear along with the volume deswelling. This microsyneresis is then fixed if during deswelling the polymer passes into the glassy state. Hence, sorbed water and the major part of sorbed methanol are contained in a separated form in induced pores, and the matrix is in fact an unswollen copolymer. On removal of the solvents by drying under conditions where the polymer is in the rubbery state, these induced pores collapse, and the corresponding volume change is included in the volume fraction of the polymer v_2 determined from the volume ratio. In this case, $1/v_2$ is not the degree of swelling of the matrix. In strongly crosslinked networks, however, the glassy transition virtually disappears, and, e.g., the specific heat continuously increases with increasing temperature up to the threshold of thermal decomposition [poly(divinylbenzene), poly(trivinylbenzene)].[21,22] The higher degree of swelling in a good solvent facilitates the condition of attaining the rubbery state during drying. This may explain great differences in changes in porosity P observed after drying of copolymers swollen in good and poor solvents (when the matrix contains a very small amount of solvent).
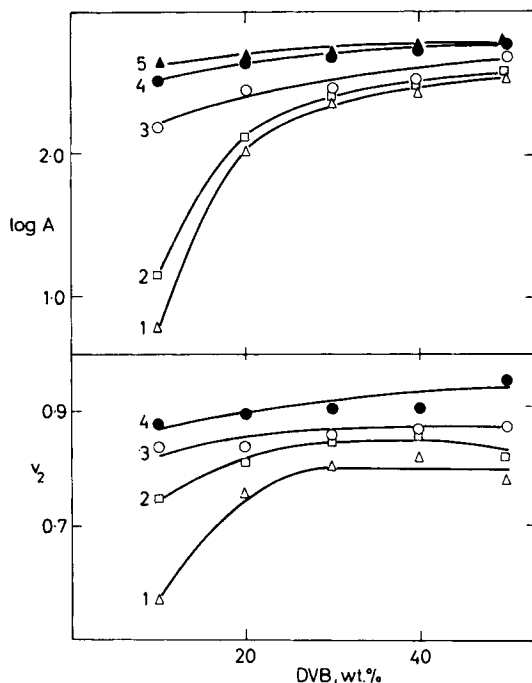

Fig. 2. Dependence of volume fraction of the polymer in the swollen state, v_2, and of the penetration modulus A (MPa) on the DVB content for samples 1–5. Samples swollen in: 1, toluene; 2, acetone; 3, methanol; 4, water; 5, dry (dried from toluene).

Thus, it should be stressed that the volume fraction of the polymer in the swollen polymer matrix may be calculated using eq. (2) only assuming isotropic swelling, with the exception of formation of induced porosity due to, e.g., the exchange of solvents. This condition is fulfilled with homogeneous samples. If, however, transient pores arising by the solvent exchange or chemically fixed pores in a weak matrix of macroporous samples collapse on drying, v_2 does not express the degree of swelling of the matrix: this degree is in fact lower (v_2 is higher). An example can be seen in a copolymer with 10% DVB prepared in the presence of octane[20]: P determined from the density of the dried sample is close to zero, while in a sample swollen in toluene small-angle X-ray scattering yields $P = 0.48$.

The penetration modulus A sensitively reacts, in the first place, to the state of copolymer—glassy or rubbery. In the latter case, A is determined by cross-linking density and by the degree of swelling. Figure 2 shows that networks in equilibrium with methanol and water and also dry networks are in the glassy state, where A is very little dependent on the DVB content. In samples swollen in acetone and especially in toluene, there is a considerable increase in the modulus with increasing DVB concentration.

The A vs. v_2 dependence in Figure 3 shows that for $v_2 \approx 0.8$, networks with 10 and 20% DVB are situated in the main transition region, and for $v_2 < 0.6$, the rubbery state has been reached. With increasing content of the crosslinking agent, the main transition is displaced toward higher degrees of swelling, but no transition could be observed in samples with a high DVB content within the given range of the degree of swelling and temperatures.

The temperature dependence of the modulus A (Fig. 3) also demonstrates that at room temperature, samples 1 with the lowest DVB content and swollen in toluene is in the rubbery state. Samples with a higher DVB content swollen in toluene exhibit a considerable decrease in the modulus with increasing temperature and thus are not in equilibrium (as also suggested by the high v_2 values of these samples, Fig. 2). Since in the rubbery region, the penetration modulus A is equal to[11] the shear modulus G, the concentration of elastically active chains
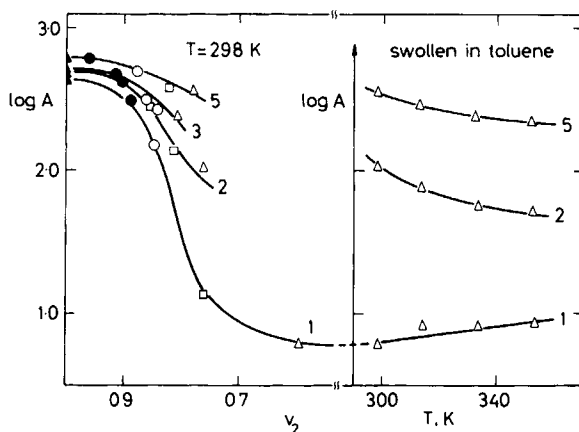

Fig. 3. Dependence of penetration modulus A (MPa) on the volume fraction of the polymer in the swollen state v_2 and on temperature T for samples 1–5. Numbers at curves correspond to the designation of samples in Table I. Samples swollen in: (●) water; (□) acetone; (△) toluene; (○) methanol; (▲) dry.

(EANC) related to the dry volume v_d can be calculated from the theory of rubber elasticity for sample 1 swollen in toluene by using the relation[23]

$$v_d = \frac{A v_2{}^{-1/3}}{\langle \alpha_0^2 \rangle RT} \tag{4}$$

where R is the gas constant, T is temperature, and $\langle \alpha_0^2 \rangle$ is the dilatation factor $[\langle \alpha_0^2 \rangle = (v^0)^{2/3}$, where v^0 is the volume fraction of the copolymer at network formation]. For sample 1, $v^0 = 1$ because it was prepared without diluent. The value $v_d = 2.9 \times 10^{-3}$ mol/cm^3 is in good agreement with the data published earlier.[7] Although the interaction parameter χ of the system S-DVB copolymer–toluene calculated using the Flory equation,[24] $\chi = 0.42$, differs from the value published earlier[7] (0.46), this difference in the χ parameter can be attributed to a small difference in v_2 ($\Delta v_2 = 0.02$), which lies at the boundary of the error of the microscopis determination of v_2.

The relative compressions at break varied between 0.3 and 0.4 and did not depend on the DVB content and swelling to any important degree. As a consequence, the stress at break σ_b reaches about one third the modulus A values and exhibit a dependence on the DVB content and on v_2 similar to that of the penetration modulus A (Table II).

Macroporous Copolymers

An interpretation of the modulus A obtained for macroporous beads is complicated by the complex character of deformation processes, because bending-type deformations become also operative here, due to buckling of the pore walls or of matrix ties connecting the separated particles. As a result, one can expect a lower modulus than is its value for matrix polymer corrected to the pore volume. The decrease in the modulus depends on the type of the pore structure. For instance, for the compression deformation of elastic foams[24,25] with spherical pores, the slope s of the E/E_0 vs. P dependence (E is the compression modulus of the foam, E_0 is the modulus of the matrix) in the limit for $P \rightarrow 0$ is[25] $-25/12 \approx -2.1$. For this reason, in macroporous samples in the rubbery state, A can be correlated with the structure of the matrix only semiquantitatively.

For samples 6–15 in the glassy state (dry and in equilibrium with water), the reduced modulus $A_d = A v_2^{-1/3}$ was found to be linearly dependent on porosity P (Fig. 4), similarly to earlier measurements.[12,13] It can be seen that the slope of this dependence, ≈ -3, is much steeper than the value corrected to the pore volume ($s = -1$). This is in agreement with results reached for model foam structures. Samples in equilibrium with water have a somewhat higher slope and a lower modulus than dry samples, which is in agreement with the assumed additionally induced porosity resulting from the exchange of solvents, on the one hand, and the collapse of some pores during drying of beads swollen with toluene, on the other. As a consequence, a large difference may exist between the porosity of dry samples obtained by drying of beads swollen in toluene and beads treated by solvent exchange. For instance, in samples with 10% DVB prepared in the presence of 50% octane, the porosity of the sample after the solvent exchange reaches 0.4–0.5 (increasing with deteriorating quality of the solvent used in the exchange), while the porosity of the sample on drying of the copolymer swollen in toluene[20] is only 0.025. At a higher content of the cross-linking agent or diluent, these differences in porosity are lower.

TABLE II
Penetration Modulus and Stress at Break for Styrene–Divinylbenzene Copolymers in Dry and Swollen States at 298 K[a]

Sample	A, MPa					σ_b, MPa				
	TOL	ACET	MET	H_2O	DRY	TOL	ACET	MET	H_2O	DRY
1	4.9	14.2	153.7	342.5	434.0	1.5	—	—		
2	107	135	280.9	458.5	494.3	52.5	52.5	104.7		
3	242	256	290.6	476.3	512.0	101.3	121.5	136.0		
4	277	293	301.0	531.2	541.0	172.5	79.2	172.9		
5	354	384	491.0	637.0	609.3	128.8	116.7	143.3		
6	35	27.8	28.8	92.1	187.9	31.7	34.8	49.1	57.5	78.4
7	48	44.5	47.8	136.9	197.4	44.5	45.6	68.4	58.7	83.1
8	37	31.4	32.4	77.0	183.3	17.8	29.0	30.1	59.6	73.9
9	34	33.4	32.9	76.0	136.6	20.3	25.9	42.5	55.8	57.0
10	34	36.0	34.7	67.6	112.7	22.7	30.3	28.6	35.8	43.7
11	127	114.6	117.4	316.4	372.9	81.6	76.1	136.3	207.8	—
12	35	27.8	28.8	92.1	187.9	31.7	34.8	49.1	57.5	78.4
13	16.5	16.2	14.2	49.9	154.7	19.2	13.9	10.7	24.5	61.6
14	6.0	5.6	5.4	19.5	163.7	5.7	9.5	5.0	11.4	59.7
15	1.0	1.0	0.9	6.9	229.6	0.7	0.8	0.9	2.8	62.1
16	34.9	27.8	28.8	92.1	187.9	31.7	34.8	49.1	57.5	78.4
17	31.7	32.5	36.3	158.5	254.1	31.6	27.9	62.7	65.6	88.5
18	21.8	22.6	36.7	199.1	281.0	17.5	32.5	70.4	70.8	116.9
19	17.2	20.6	64.7	361.7	333.8	12.2	56.4	96.0	119.2	128.5
20	13.9	19.3	75.4	404.2	362.7	68.1	70.4	85.0	111.4	80.1

[a] TOL = Toluene; ACET = acetone; MET = methanol; DRY = dry state.
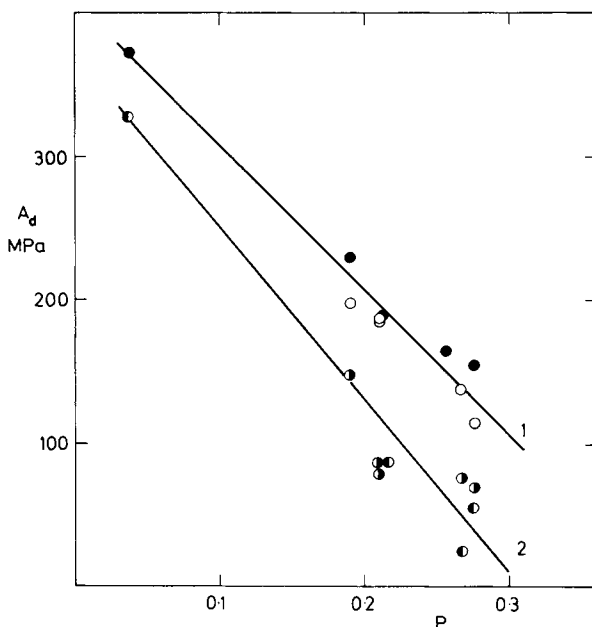
Fig. 4. Dependence of reduced modulus $A_d = A v_2^{-1/3}$ on porosity P.   Curve, 1 dry samples: (O)
sample 6–10; (●) sample 11–15.   Curve 2, samples in water: (◐) sample 6–10; (◑) sample 11–15.

The results obtained with samples 6–10 show (Tables I and II) that at a high
DVB content the properties of the beads do not depend too much on the ther-
modynamic quality of the diluent.   As assumed, porosity increases slightly with
deteriorating thermodynamic quality of the diluent, similarly to v_2, but the
modulus A does not change too much.   A noteworthy finding is that A and v_2
are independent of the swelling medium on transition from toluene through
acetone to methanol, which corresponds both to empirical experience and to
predictions ensuing from the phase separation theory, viz., that at a high content
of the crosslinking agent the threshold of separation and the ratio of the phase
volumes (porosity) are mainly determined by the volume fraction of the diluent
and much less by its thermodynamic quality.   Samples in equilibrium with water
have a higher modulus than samples in contact with the remaining three solvents;
the main cause seems to be that water does not penetrate into fine pores owing
to the hydrophobicity of the polymer, but only removes the diluent, and the re-
sulting change in the interfacial energy may lead to the collapse of these
pores.

The increasing content of the crosslinking agent changes drastically the co-
polymer structure (series 11–15, Table II).   The dependence of the modulus A
on temperature of the beads in toluene (Table III) (a slight decrease) does not
allow us to affirm unambiguously whether the matrix is in the rubbery state or
not.   The steep drop in the modulus of the copolymers with increasing dilution
at polymerization found for samples in contact with toluene, acetone, and
methanol is attributable rather to a change in the porous structure than to a
change in the structure of the matrix.   The value of P at high dilution does not
to any extent express porosity in the swollen state, and the low v_2 values are
mainly a consequence of the partial collapse of the structure on drying.   In this

TABLE III
Temperature Dependence of Penetration Modulus for Styrene–Divinylbenzene Copolymers in Swollen State

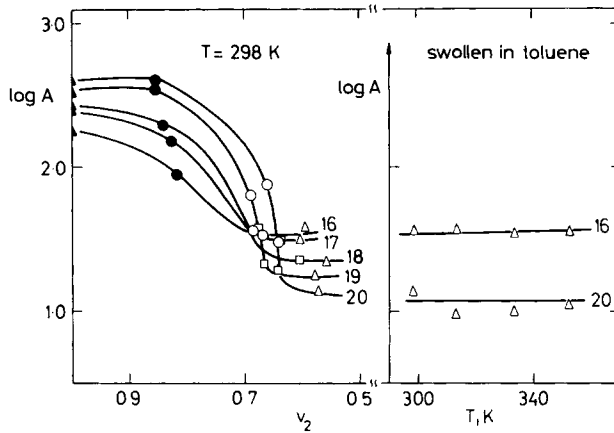| Sample	A in toluene, MPa				A in H₂O, MPa				
	298 K	313 K	333 K	353 K	298 K	313 K	333 K	353 K	368 K
1	6.03	9.0	7.9	8.6	342.5	343.9	229.1	120.2	106.4
2	106.7	78.4	56.0	54.0	—	—	—	—	—
5	353.7	296.4	246.9	225.0	637.8	546.6	334.2	312.6	310.3
12	34.9	35.1	33.2	24.0	92.1	83.1	74.8	72.6	60.9
13	16.5	12.2	14.4	13.2	49.9	49.6	41.6	30.3	23.1
14	5.96	5.10	5.18	4.60	19.5	28.6	17.8	18.6	13.4
15	1.01	1.05	—	—	—	—	—	—	—
20	13.9	9.2	9.8	10.5	404.2	294.5	207.5	215.9	166.0

Fig. 5. Dependence of penetration modulus A (MPa) on volume fraction of the polymer in the swollen state v_2 and on temperature T for samples 16–20. Numbers at curves correspond to the designation of samples in Table I. Samples swollen in: ($\triangle$) toluene; ($\square$) acetone; ($\bigcirc$) methanol; ($\bullet$) water; ($\blacktriangle$) dry.

connection, one should note the extremely low v_2 for sample 15 in water. It is known that at such high dilutions the pore structure is loose, consisting of rather weakly joined microgel particles.[14,15] Deformation is produced predominantly by buckling of these ties. Certainly, dilution has some effect also on the structure of the matrix because it increases cyclization and reduces the degree of polymerization of the primary chains, but we believe that these effects are of secondary importance.

The results obtained in the measurements on samples 16–20 demonstrate (Table II) that with increasing DVB concentration and at the same dilution, the permanent porosity in the dry state increases and the matrix becomes more rigid. For example, the modulus A of sample 16 with 50% DVB is again little dependent on the type of the solvent, because the matrix itself does not swell too much; while if the DVB concentration decreases to 10%, the lightly crosslinked matrix already sensitively reacts to the thermodynamic quality of the solvent. Of course, porosity in the swollen state depends on the DVB concentration, similarly to the tendency of the pores to collapse on drying.

The gradual weakening of the effect of porosity P on the modulus A, when the copolymers pass from the glassy into the rubbery state, may be seen in Figure 5 for samples 16–20. While in the dry state and for beads in equilibrium with water, porosity has a decisive influence on A (the effect of DVB is opposite to that observed for homogeneous networks, Fig. 3), for samples swollen in toluene and acetone, the A values are mainly determined by the DVB content. The temperature dependence of A also infers that the matrix of beads in toluene and acetone is in the rubbery state, and the A values increase markedly in both solvents with increasing DVB content.

It seems of interest to compare the modulus of the macroporous copolymer 20 with the corresponding homogeneous copolymer 1 (both contain 10% DVB). Their behavior suggests that on swelling in toluene, both copolymers are in the rubbery state. Then the considerably higher modulus of sample 20 is quite surprising, even if it could be expected that increased porosity and cyclization should have an opposite effect. The result, however, is not at variance with the

assumed mechanism of phase separation and with earlier data.[2,9,10] After phase separation, the separated polymeric phase increases during further polymerization owing to the diffusion and polymerization of monomers inside this phase, its volume increases, and a composite expanded network is formed, with a modulus higher than that of a homogeneous network with the same content of the crosslinking agent.[9]

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