Die Angewandte Makromolekulare Chemie **157** *(1988) 1 – 13 (Nr. 2594)*

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Styrene-Divinylbenzene Copolymers*

VI. Porosity Formation in the Presence of Toluene-Cyclohexanol Mixtures as Inert Diluents

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(Received 29 June 1987)

SUMMARY:

Porosity formation by suspension copolymerization of styrene-divinylbenzene (S-DVB) in toluene-cyclohexanol mixtures was investigated. The total porosity of the copolymers increases and their volume swelling ratio in toluene decreases as the DVB concentration in the starting monomer mixture increases and the solvating power of the polymerization medium decreases. The volume fraction of the diluent separated out of the network phase, v_D, was found to be constant after passing a critical amount of DVB and the diluent. The limiting value of v_D is only dependent on the solubility parameter difference of the polymer and the diluent. Thus, if sufficient amounts of DVB and diluent are present during the network formation, the maximum porosity of S-DVB copolymers can be predicted from the solubility parameters of the components.

ZUSAMMENFASSUNG:

Die Porositätsbildung bei der Suspensionscopolymerisation von Styrol/Divinylbenzol (S-DVB) in Toluol-Cyclohexanol-Mischungen wurde untersucht. Die Porosität der Copolymeren wächst, und ihr Quellverhalten nimmt ab, wenn der DVB-Gehalt in der Ausgangsmischung ansteigt und die Lösefähigkeit des Mediums abnimmt. Es wurde gefunden, daß der Volumenbruch des aus dem Netzwerk ausgeschiedenen Lösemittels, v_D, konstant wird, wenn eine kritische Menge an DVB und Lösemittel überschritten ist. Dieser Grenzwert für v_D ist nur vom Lösungsparameterunterschied zwischen Lösemittel und Polymerem, abhängig. So kann, wenn genügende Mengen an DVB und Lösemittel zugegen sind, die maximale Porosität der S-DVB-Copolymeren aus den Lösungsparametern der Komponenten vorausgesagt werden.

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* Part V: cf.[5].

0003-3146/88/$03.00

Introduction

Preparation of porous styrene-divinylbenzene (S-DVB) copolymer beads has received considerable attention in the last 30 years[1-4]. Porous S-DVB copolymers have been prepared from the monomers in the presence of an inert (non-polymerizable) diluent. The inert diluent present during the network formation may remain in the network (gel) phase throughout the copolymerization, resulting in the formation of expanded networks, or may separate out of the network phase, resulting in the formation of porous copolymers. The distribution of the diluent between network and diluent phases at the end of the copolymerization determines the total porosity of the resulting copolymers and their volume swelling ratio in solvents. The relation between these two important properties of a heterogeneous network to the composition of the starting monomer mixture is given by[5]

$$v_2 = \frac{d_2/d_0}{1/v_{2,st} + r\, d_{2,r}/d_M} \tag{1}$$

where v_2 is the volume fraction of copolymer in the swollen gel, $v_{2,st}$ is the value of v_2 for the corresponding standard (homogeneous) copolymers, d_0 is the apparent density of the copolymer, r is the diluent-monomer volume ratio in the starting monomer mixture, d_M, d_2, and $d_{2,r}$ are the densities of the monomers, homogeneous copolymer, and copolymer in the rubbery state, respectively.

The dependence of v_2 and d_0 on the composition of the monomer mixture is also given in Fig. 1, which shows that, for a given composition of the starting monomer mixture ($v_{2,st}$ and r are taken to be constant), v_2 varies between two limiting values depending on the apparent density of the copolymers[5], i.e., between A and A′ or B and B′. Thus, Eq. (1) can also be written as

$$d_0\, v_2 = d_{0,min}\, v_{2,st} \tag{2}$$

where $d_{0,min}$ is the minimum value for d_0 which can be achieved if $v_2 = v_{2,st}$, i.e., if all the diluent separates out of the network phase. $d_{0,min}$ values are located in the stippled surface of Fig. 1, and can be calculated as follows:

$$d_{0,min} = \frac{d_2}{1 + r\, v_{2,st}\, d_{2,r}/d_M} \tag{3}$$

Moreover, the location of v_2 or d_0 at a given DVB concentration and dilution, i.e., the distribution of the swelling agent between gel and pore portions of the network, depends on the solvating power of the diluent. In a previous work, two types of solvents were used as the diluents in the polymerization system[6]. The first, represented by toluene, has the same thermodynamic properties as the monomers, and thus, the overall solvating power of the diluent-monomer mixture is essentially constant throughout the copolymerization. The other type, represented by cyclohexanol, is a non-

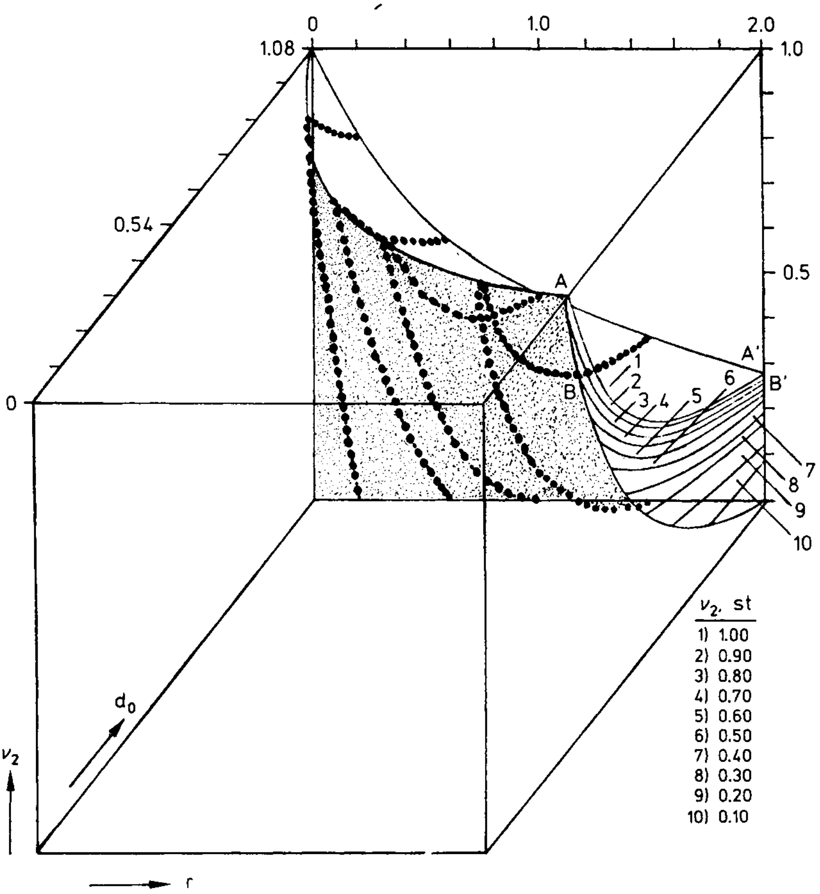

Fig. 1. Dependence of v_2 and d_0 on the composition of the starting monomer mixture according to Eq. (1)[5]. During the calculations, the values d_2, $d_{2,r}$, and d_M used were 1.08, 1.09, and 0.91 g/cm^3, respectively.

solvent for polystyrene and the overall solvating power of the diluent-monomer mixture for the polymer decreases as the monomers are consumed in the polymerization. It was found that during the copolymerization, toluene remains in the network phase up to 15 – 25 wt.-% DVB, whereas cyclohexanol separates out totally of the network phase at 15 wt.-% DVB ($r = 1.00$)[6]. In the intermediate situations, the diluent is distributed between the network and diluent phases.

This study attempts to explain the distribution of the diluent between gel and pore portions of the final network, depending on the solvating power of the medium. For this purpose, both of the diluents, namely toluene and cyclohexanol, were used together in the polymerization system in various volume fractions and compositions. The degree of swelling in toluene as well as the apparent density of the resulting copolymers were examined as a function of the DVB concentration, diluent composition and dilution.

It must be pointed out that the pore structure of S-DVB copolymers may change during drying and the copolymers in a dried state do not necessarily reflect the actual pore structure formed during the synthesis[6–14]. In this study, the swollen copolymers were treated with solvents with decreasing solvating power before the drying process in order to develop the actual pore structure[6]. In this way, the swollen state porosity, i.e., the maximum porosity of the copolymers was preserved in the dried state.

Experimental

All monomers and reagents were purified and distilled prior to use. The GC analysis of DVB gave the following results: 55.3% DVB isomers (m-DVB: p-DVB ratio 3.3 : 1), 43.4% ethylvinyl benzene and 1.3% nonpolymerizable compounds. The diluents, toluene (Merck) and cyclohexanol (Fluka), were used as received.

The S-DVB copolymer beads were obtained by the suspension polymerization method, as described previously[15]. Toluene-cyclohexanol mixtures were used as the diluent of the organic phase. The volume fraction of cyclohexanol in the diluent mixture, $v_{CH\text{-}OH}$, was taken as 0.50 and 0.75 throughout the study. The diluent-monomer volume ratio, r, was varied between 0.73 and 4.00, the DVB concentration between 5 mol-% and 30 mol-%. After polymerization, the copolymer beads of 0.35 – 1.00 mm in diameter were extracted with acetone for 16 h and then were swollen to equilibrium in toluene at room temperature. The swollen copolymers were then successively washed with solutions whose compositions were changed gradually from toluene to pure acetone and then progressively to pure methanol and finally to pure water. The samples after the treatment with water as a final solvent were dried in vacuo at room temperature.

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method. The porosity, P (%), was calculated from d_0 as:

$$P = (1 - d_0/d_2) \times 100 \tag{4}$$

The weight swelling ratio in toluene, q_w, was determined by the centrifugation method. The volume fraction of copolymer in the swollen gel, v_2, was calculated as follows[16]:

$$v_2 = \frac{d_2/d_0}{1 + (q_w - 1)\, d_{2,r}/d_1} \tag{5}$$

During the calculations, the values d_2, $d_{2,r}$, d_1, and d_M used were 1.08, 1.09, 0.867, and 0.91 g/cm^3, respectively. $v_{2,st}$ values were taken from the literature[6].

Results and Discussion

The Influence of the DVB Concentration and the Diluent Composition

The composition of the copolymers prepared at a fixed dilution ($r = 1.00$) and their properties are given in Tab. 1. In Fig. 2, the change in the apparent density of the copolymers, d_0, is plotted against the DVB concentration. The solid curve represents the minimum apparent density values, $d_{0,\min}$, calculated using Eq. (3). The experimental data points for $v_{CH-OH} = 1.00$ were taken from the literature[6]. Fig. 2 shows that, for a given value of v_{CH-OH}, d_0 decreases with increasing DVB concentration and eventually reaches an approximately constant value after a critical amount of DVB. d_0 also decreases with increasing cyclohexanol content of the diluent mixture, at a given DVB concentration. Moreover, with the exception of the copolymers prepared at $v_{CH-OH} = 1.00$ and equal to more than 12.5 mol-% DVB, d_0 remains below $d_{0,\min}$ indicating that the separated copolymers during the network formation process are more or less swollen with the diluent-monomer mixtures.

The volume swelling ratio of the copolymers in toluene is given in Fig. 3 in terms of v_2 as a function of the DVB concentration. The dotted curves represent the calculated v_2 values using Eq. (1). As expected, v_2 increases with increasing DVB concentration and with increasing cyclohexanol content in the diluent mixture. The calculated v_2 values for $v_{CH-OH} = 0.75$ are in good agreement with the experimental data points. For $v_{CH-OH} = 0.50$, however, the experimental determined v_2 values remain significantly over the theoretical ones. This is believed to be primarily due to the loss of

Tab. 1. Composition and properties of copolymers prepared at r = 1.00[a].

DVB (mol-%)	v_{CH-OH}	d_0 (g/cm^3)	P (%)	v_2	$(v_2)_{calcd.}$	v_D
				in toluene		
5	0.50	1.04	4	0.40	0.33	0.06
	0.75	1.02	6	0.40	0.34	0.10
10	0.50	1.02	6	0.50	0.40	0.07
	0.75	0.76	30	0.55	0.53	0.51
15	0.50	0.97	10	0.53	0.435	0.13
	0.75	0.67	38	0.66	0.63	0.70
20	0.50	0.845	22	0.63	0.51	0.31
	0.75	0.63	42	0.70	0.68	0.78
25	0.50	0.825	24	0.64	0.53	0.33
	0.75	0.62	43	0.73	0.70	0.80
30	0.50	0.795	26	0.68	0.55	0.37
	0.75	0.61	44	0.71	0.72	0.80

[a] v_{CH-OH} = Volume fraction of cyclohexanol in the diluent mixture, d_0 = apparent density and P(%) = total porosity of copolymers, v_2 = volume fraction of copolymer in the swollen gel, $(v_2)_{calcd}$ = calculated v_2 values using Eq. (1), v_D = volume fraction of the diluent separated out of the network phase.

the diluent during the polymerization, i.e., by the solubility of the diluent in the aqueous phase or by evaporation.

The volume fraction of the diluent separated out of the network (gel) phase, v_D, can be calculated as[5]

$$v_D = \frac{v_2 - v_{2,\mathrm{min}}}{v_{2,\mathrm{st}} - v_{2,\mathrm{min}}} = \frac{1/d_0 - 1/d_2}{1/d_{0,\mathrm{min}} - 1/d_2} \tag{6}$$

where $v_{2,\mathrm{min}}$ is the minimum v_2 value calculated for $d_0 = d_2$ using Eq. (1). The dependence of v_D on the DVB concentration is given in Fig. 4. v_D increases with increasing DVB concentration and then remains constant above a critical value of the DVB. v_D also increases with increasing cyclohexanol content of the diluent mixture. In the presence of a sufficient amount of DVB, the values d_0 and v_D do not change with a further increase in the DVB concentration, as seen in Fig. 2 and Fig. 4. The limiting d_0 and v_D are given in Tab. 2 together with the corresponding critical DVB concentrations. The results show that the critical DVB concentration decreases with increasing cyclohexanol content of the diluent mixture, i.e., with decreasing solvating power of the polymerization medium.

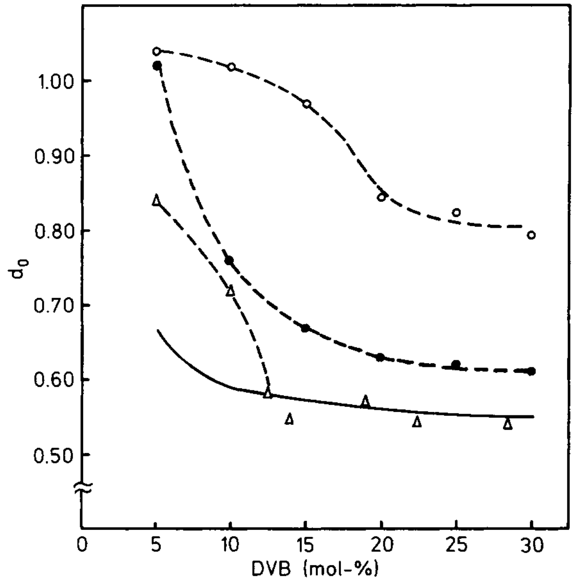

Fig. 2. Dependence of the apparent density, d_0, on the DVB concentration for copolymers prepared at r = 1.00 and v_{CH-OH} = 0.50 (○), 0.75 (●), and 1.00 (△). The solid curve represents $d_{0,\min}$ values calculated using Eq. (3).

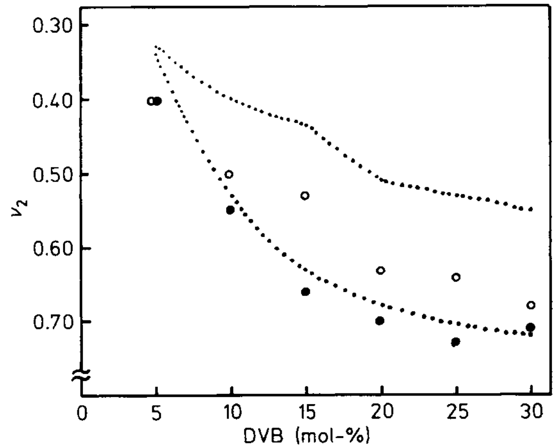

Fig. 3. Dependence of v_2 on the DVB concentration for copolymers prepared at r = 1.00 and v_{CH-OH} = 0.50 (○) and 0.75 (●). The dotted curves represent the calculated v_2 values using Eq. (1).

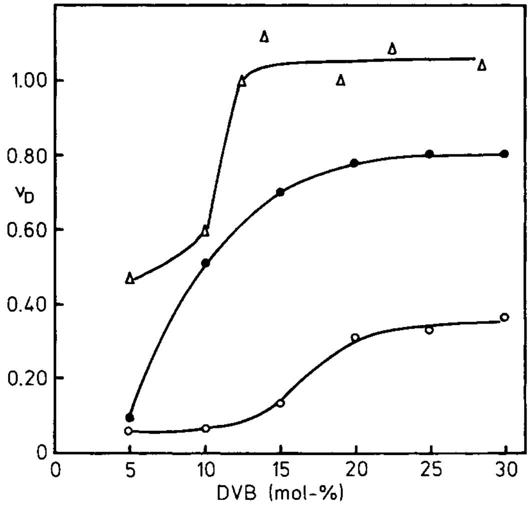

Fig. 4. Dependence of the volume fraction of the diluent separated out of the network phase, v_D, on the DVB concentration for copolymers prepared at r = 1.00 and v_{CH-OH} = 0.50 (○), 0.75 (●), and 1.00 (△).

Tab. 2. Limiting values of d_0 and v_D, and the corresponding critical DVB concentrations for copolymers prepared at r = 1.00.

v_{CH-OH}	$(DVB)_{crit}$ (mol-%)	d_0 (g/cm^3)	v_D
0.50	20–25	0.81	0.35
0.75	20	0.62	0.80
1.00	12.5	0.56	1.0

It is known that the process of solution is governed by the free energy equation

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

where ΔG is the change in Gibb's free energy, ΔH is the heat of mixing, T is the absolute temperature, and ΔS is the entropy of mixing. A negative ΔG

predicts that the solution process will occur spontaneously. Since the value of ΔS in a solution process is always positive, the magnitude of the heat term ΔH is the deciding factor in determining the sign of the free energy change. According to the Hildebrand theory[17], the heat of mixing is dependent on the square of the difference of the solubility parameters for the two components. Thus, the solubility of a polymer in a solvent is favoured when the heat term in Eq. (7) is minimized, i.e., when the solubility parameters of the two components are most closely matched. If δ_l and δ_2 are the solubility parameters for the solvent and the polymer, respectively, the solvating power of the medium can be estimated from $(\delta_l - \delta_2)^2$.

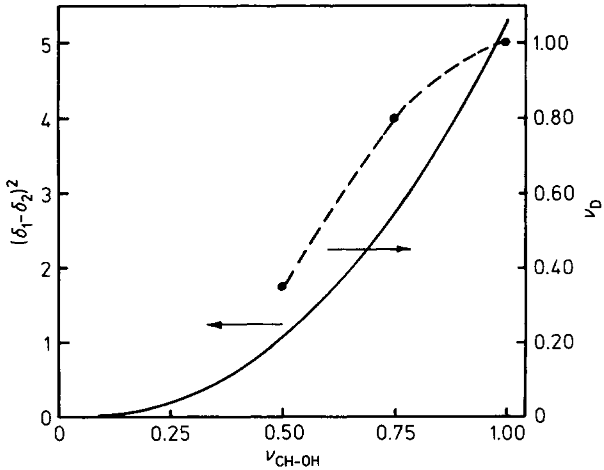

Fig. 5. Dependence of $(\delta_l - \delta_2)^2$ and the limiting v_D on the volume fraction of cyclohexanol in the diluent mixture (v_{CH-OH}).

In Fig. 5, $(\delta_l - \delta_2)^2$ for S-DVB copolymer-toluene-cyclohexanol system and the limiting v_D are plotted against the cyclohexanol content of the diluent mixture. The solubility parameter of the diluent mixture, δ_l, was calculated as

$$\delta_l = (\delta_{CH-OH} - \delta_T)\, v_{CH-OH} + \delta_T \tag{8}$$

where δ_{CH-OH} and δ_T are the solubility parameters of cyclohexanol and toluene, respectively. During the calculations, the values δ_{CH-OH}, δ_T, and δ_2 used were[18] 11.4, 8.9, and 9.1 $(cal/cm^3)^{0.5}$, respectively. It must be pointed out that the monomers, styrene and DVB, are thermodynamically good solvents for polystyrene and thus, the unreacted monomers during the copolymerization raise the solvating power of the diluent mixture. But, this effect is not included in the calculations since the value v_D at the end of the polymerization is not affected by it. With increasing volume fraction of cyclohexanol in the diluent mixture from 0.50 to 1.00, the value $(\delta_1 - \delta_2)^2$ increases drastically (Fig. 5). Similarly, an abrupt increase in v_D was observed in this range. Thus, if sufficient amounts of DVB are present during the copolymerization, the extend of the phase separation is only dependent on the thermodynamic interaction of polystyrene with the diluent used.

The Influence of the Dilution

A series of copolymers was prepared with 20 mol-% DVB and at $v_{CH-OH} = 0.75$, but with different degrees of dilution. The composition of the copolymers and their properties are given in Tab. 3. The apparent density of these copolymers is plotted against the diluent-monomer volume ratio, r, in Fig. 6, which shows that the apparent density decreases with increasing dilution of the monomers.

Tab. 3. Composition and properties of copolymers prepared with 20 mol-% DVB and at $v_{CH-OH} = 0.75$.

r	d_0 (g/cm^3)	P (%)	v_2 in toluene	$(v_2)_{calcd.}$ in toluene	v_D
0.73	0.985	9	0.57	0.50	0.15
1.00	0.630	42	0.70	0.68	0.79
1.50	0.566	48	0.70	0.61	0.67
2.00	0.406	62	0.71	0.72	0.92
3.00	0.336	69	0.64	0.65	0.82
4.00	0.315	71	0.53	0.56	0.67

As shown in the previous section, the copolymer prepared at r = 1.00 contains a sufficient amount of DVB to reach the limiting value of v_D (Tab. 1 and Fig. 4). If we assume that the limiting v_D does not change with increasing dilution, all other copolymers given in Tab. 3 must also have the same v_D values. Indeed, the v_D values for 5 copolymer samples with $r \geq 1.00$

gave a mean $\nu_D = 0.77$ with a standard deviation of 0.10. Furthermore, the apparent density of these copolymers can be calculated from the limiting ν_D using Eqs. (6) and (3) as

$$d_0 = \frac{d_2}{1 + r\nu_{2,st}\, d_{2,r}\, \nu_D/d_M} \tag{9}$$

The dotted curve in Fig. 6 represents the calculated d_0 values using Eq. (9) (the values $\nu_{2,st}$ and ν_D used were 0.76 and 0.8, respectively).

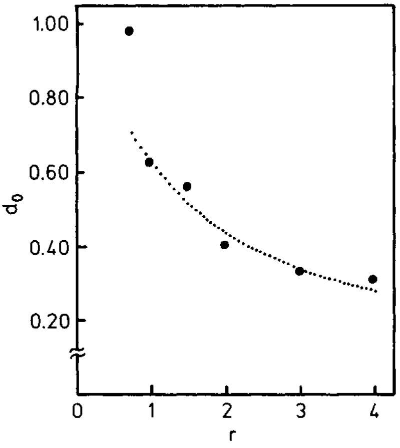

Fig. 6. Dependence of the apparent density, d_0, on the diluent-monomer volume ratio, r, for copolymers prepared with 20 mol-% DVB and at $\nu_{CH-OH} = 0.75$. The dotted curve represents the calculated d_0 values using Eq. (9).

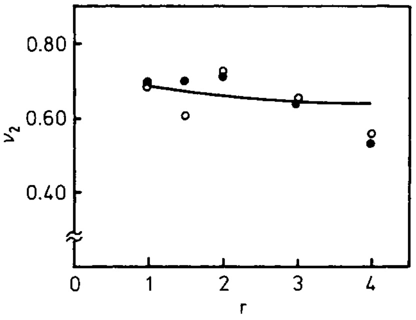

Fig. 7. Dependence of ν_2 on the diluent-monomer volume ratio, r, for copolymers prepared with 20 mol-% DVB and at $\nu_{CH-OH} = 0.75$. The solid curve represents the calculated ν_2 values for $\nu_D = 0.8$.

With one exception, the experimental d_0 values are in good agreement with the calculated values. The deviation at $r = 0.73$ may be due to the insufficient amount of the diluent present during the network formation. It may thus be concluded that the limiting value of ν_D is independent on the degree of dilution, and, if sufficient amounts of DVB and diluent are present during the network formation, the porosity of the copolymers can be predicted from the limiting ν_D which is only dependent on $(\delta_1 - \delta_2)^2$.

The swelling ratio of the copolymers in toluene is given in Fig. 7 in terms of ν_2 as a function of dilution for $r \geq 1.00$. The theoretical prediction for $\nu_D = 0.8$ is shown with the solid curve and the calculated ν_2 values using Eq. (1) are represented by open circles. Fig. 7 shows that the value ν_2 does not change appreciably with increasing dilution of the monomers. Some deviations from the theoretical prediction for $\nu_D = 0.8$ were observed, particularly at $r = 2.00$ and 4.00.

Conclusions

As expected, the total porosity of S-DVB copolymers increases and their volume swelling ratio in toluene decreases as the DVB concentration in the starting monomer mixture increases and the solvating power of the polymerization medium decreases.

The volume fraction of the diluent separated out of the network phase, ν_D, was found to be constant after passing a critical amount of DVB and the diluent. The limiting value of ν_D is only dependent on the solubility parameter differences of the polymer and the diluent. Thus, if sufficient amounts of DVB and diluent are present during the network formation, the maximum porosity of the resulting copolymers can be predicted from the solubility parameters of the components.

The author wishes to thank Mr. Ihsan Ülgen for technical assistance during this work.

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