

Phase Separation in the Synthesis of Styrene-Divinylbenzene Copolymers with Di-2-Ethylhexyl Phthalate as Diluent

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Synopsis

Phase separation by suspension copolymerization of styrene-divinylbenzene (DVB) with di-2-ethylhexyl phthalate (DOP) as diluent was investigated using equilibrium swelling, swelling rate, apparent densities, and mercury porosimetry. The copolymer prepared in the absence of DOP is heterogeneous, showing that a phase separation exists in the polymerization system, and, in the presence of DOP, the propagating copolymer separates earlier. Furthermore, with increasing amounts of DVB, phase separation occurs earlier than gelation, which causes a sudden increase in the amount of pores about 200–500 Å in diameter corresponding to the interstices between the microspheres.

INTRODUCTION

Syneresis and formation of heterogeneous (porous) structures in styrene-divinylbenzene (DVB) copolymer-diluent systems during crosslinking may be regarded as phase separation.¹ The degree of phase separation is dependent on the concentration of the crosslinking agent, concentration of the diluent, and the reaction temperature. There are three types of diluents used to prepare porous matrices²: (1) solvating diluents such as toluene and dichloroethane, (2) nonsolvating diluents such as *n*-heptane and *n*-butyl alcohol, and (3) linear polymers, e.g., polystyrene. Hohenstein and Mark³ reported in 1946 the formation of soft and resilient products by adding a plasticizer to monomer-swollen crosslinked beads. Recent studies performed with phthalate plasticizers as diluent, demonstrated the formation of macroporous styrene-DVB copolymers.^{4,5} In this study, a number of styrene-DVB copolymers with various concentrations of DVB (from 4 wt % to 32 wt % of the monomers) and di-2-ethylhexyl phthalate (DOP) (from 0 to 0.48 volume fraction of the organic phase) as diluent were prepared. The degree of phase separation related to the DOP concentration and crosslinking density has been examined by mercury porosimetry and swelling experiments with toluene. Our aim was primarily to check if there were significant differences in the behavior of DOP as diluent; but it is also of inherent interest to have precise data on the change of the pore structure during the transition from homogeneous to heterogeneous gelation.

EXPERIMENTAL

Materials

All monomers and reagents were purified and distilled prior to use. The GC analysis of DVB gave the following result: 13.8 wt % *p*-DVB, 40.6 wt % *m*-DVB, 43 wt % ethylvinylbenzene, and 2 wt % nonpolymerizable compounds. The diluent, DOP (Plastifay Chem. Co.) was used as received (> 99% in purity).

The styrene-DVB copolymers were obtained by the suspension polymerization method. Dibenzoyl peroxide as the initiator (1.26 wt % in relation to the monomers) was dissolved in the selected monomer-DOP mixture and this (a volume between 45 and 90 cm³ depending on composition) was then added to a solution of bentonite (0.2 g), gelatine (0.46 g), and NaCl (0.8 g) in 200 cm³ water at 80°C and 250 rpm. The reaction was allowed to proceed for 16 h. After polymerization, the copolymer beads were washed with water and dried *in vacuo* at 60°C, and then extracted with acetone for 24 h and finally dried *in vacuo* at 60°C. Yields were essentially above 90% to give spherical beads of 0.35–1.0 mm in diameter.

Methods

The apparent density of the copolymers, d_0 , was determined by the mercury pycnometric method.⁶ Pore size distribution of the copolymers was determined by mercury porosimetry with an Aminco porosimeter. The mercury penetrometer used had an upper pressure limit of 30,000 psi, and thus only pores of equivalent diameters greater than 60 Å were sensed. Porosity, $P\%$, was calculated as

$$P\% = V_p d_0 \times 100\% \quad (1)$$

where V_p is the cumulative pore volume obtained from pore size distribution.

The weight swelling ratio in toluene was determined by the centrifugation method.⁷ The volume fraction of copolymer in the swollen gel, ν_2 , was calculated from the weight swelling ratio with an equation given by Beranova and Dusek⁸ and Wieczorek et al.⁹ The swelling rate was determined by placing the dried copolymer in a graduated cylinder and reading the volume. An excess of toluene was added, and the volume was read periodically until the copolymer had ceased to swell. Percentage of swelling at a predetermined contact time was calculated as

$$\frac{\text{final volume} - \text{initial volume}}{\text{initial volume}} \times 100\% \quad (2)$$

The composition of the copolymers and their properties are given in Table I. The DVB concentration was varied between 4 wt % and 32 wt %, because above 32 wt % the mechanical strength of the DOP-modified copolymers is too weak to withstand measurements of pore structure. The DOP concentration was also limited since it is not completely extracted at high concentrations.

TABLE I
 Composition and Properties of Copolymers^a

Sample no.	DVB (wt %)	v_2^0	v_2 (in toluene)	$d_0 \times 10^{-3}$ (kg/m ³)	P (%)		
					I	II	(I + II)
1	15	1.00	0.73	1.06	1.26	2.37	3.63
2	15	0.81	0.65	1.02	1.05	7.55	8.60
3	15	0.69	0.52	1.00	1.07	8.65	9.72
4	15	0.52	0.39	1.02	2.48	4.62	7.10
5	4	0.52	0.27	1.03			
6	8	0.52	0.33	1.07	1.39	4.34	5.73
7	15	0.52	0.39	1.02	2.48	4.62	7.10
8	18	0.52	0.43	0.98	3.10	10.17	13.27
9	22	0.52	0.67	0.61	4.43	43.21	47.64
10	32	0.52	0.78	0.59	1.98	40.10	42.08 ^b

^a v_2^0 = initial volume fraction of the monomers in the organic phase, v_2 = volume fraction of copolymer in the swollen gel, d_0 = apparent density of copolymer, and P (%) = porosity from pores larger than 1700 Å (I) and thus between 70 and 1700 Å (II).

^b Pores of equivalent diameter greater than 90 Å (20,000 psi) were measured.

RESULTS AND DISCUSSION

Homogeneous Gelation

The results obtained from samples 1–4 show (Table I) that at 15 wt % DVB, with one exception, the porosity increases slightly with the volume fraction of the diluent in the organic phase. The decrease of the porosity in sample 4 may be a consequence of incomplete extraction of DOP; in the distribution curve of this sample the pores less than 70 Å in diameter do not appear and indicate the plugging of the smaller pores by the diluent (Fig. 3).

As the volume fraction of DOP is increased at a fixed DVB content, there is a decrease in v_2 and an increase in the swelling rate of copolymers (Table I and Fig. 1). The dependence of the DOP content on v_2 in toluene is linear and is similar to the Millar equation¹⁰:

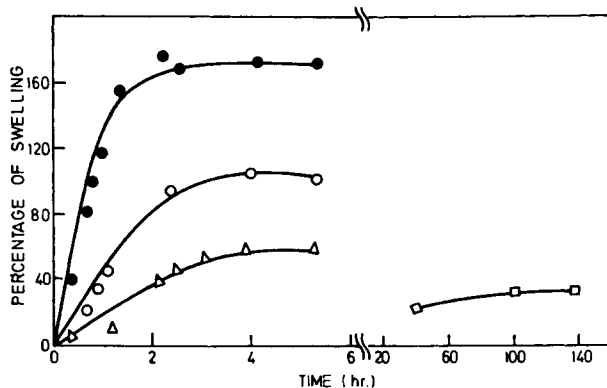


Fig. 1. Dependence of the swelling rate and the swelling ratio of the copolymers on the volume fraction of DOP (1 - v_2^0): DVB: 15 wt %; v_2^0 : 0.52 (●); 0.69 (○); 0.81 (△); 1.00 (□).

$$U = U_0 + kD \quad (3)$$

where U is the equilibrium volume of toluene per unit mass of dry copolymer $[(1 - \nu_2)/\nu_2]$, U_0 is the corresponding value for a copolymer prepared without diluent, D is the volume of DOP per unit mass of monomers $[(1 - \nu_2^{(0)})/\nu_2^{(0)}]$, and k is a constant, which was found to be 1.35 (Fig. 2).

The lower ν_2 values with increasing dilution are mainly a consequence of the increasing ratio of cyclization leading to elastically wasted links, and of the reduction of the polymerization degree of the primary chains. This is a well-known phenomenon in homogeneous gelation.

Figure 3 illustrates pore size distribution for these copolymers as given in differential and integral mode. It seems that the copolymer prepared without using DOP is heterogeneous, showing that a phase separation exists in the polymerizing system. When DOP was added, the amount of pores around 70–1700 Å in diameter increased, indicating that the propagating copolymer was separated out of the monomer mixture earlier than in the previous case. In all cases equivalent pore diameters of about 70, 120, and 160–220 Å were measured. Results in Table I show that with increasing DOP concentration the amount of pores larger than 1700 Å in diameter remain constant (except sample 4), but their diameter becomes smaller and smaller, becoming closer to 1700 Å as the DOP content increases.

As described by Kun and Kunin,¹¹ the formation of the pore structure can be divided into three stages. During the first stage intramolecularly crosslinked polymer microgels are formed that are soluble in the monomer-diluent system. When the solvating monomers are converted into copolymer, the polymer chains become less swollen and will become entangled by continuing polymerization. This yields the "nuclei" suggested by Sederel and DeJong.¹² In the second stage of pore structure formation, the entanglement continues, and the nuclei are aggregated in microspheres. In the third stage, the microspheres are aggregated in particles more or less separated by large holes.

From the experimental data, it may be estimated that the amount of microspheres increases with increasing DOP concentration at a fixed DVB

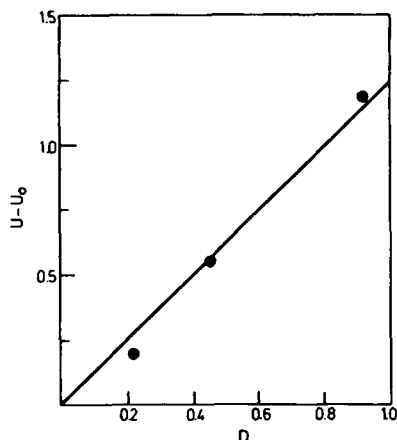


Fig. 2. Plot for swelling equation: $U = U_0 + kD$.

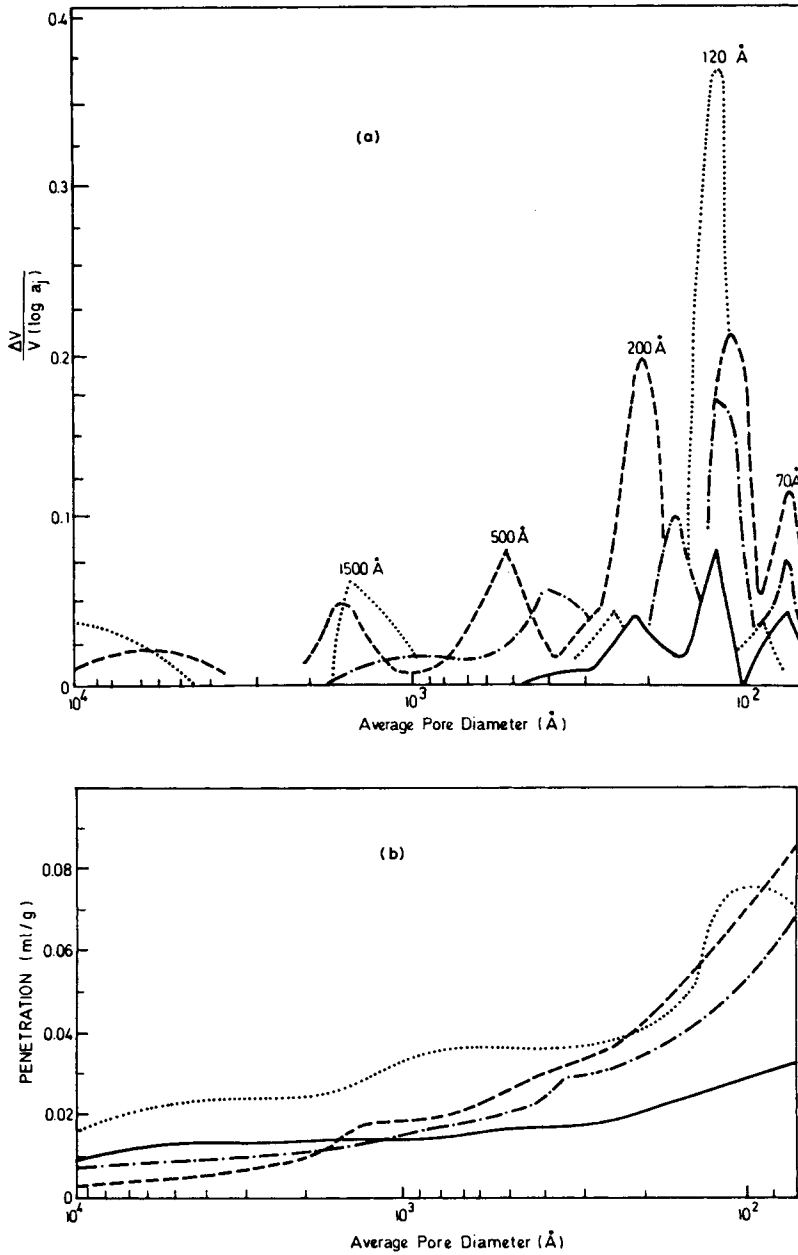


Fig. 3. Pore size distribution of copolymers prepared with 15 wt % DVB and various amounts of DOP in differential (a) and in integral mode (b); v_2^0 : 1.00 (-); 0.81 (-.-); 0.69 (-.-.); 0.52 (· · ·).

content. Thus, it is evident that DOP promoted phase separation of copolymers formed in the homogeneous gelation.

Transition to the Heterogeneous Gelation

Figure 4 shows the dependence of the apparent density and the porosity of copolymers on the DVB concentration at a fixed amount of DOP. With

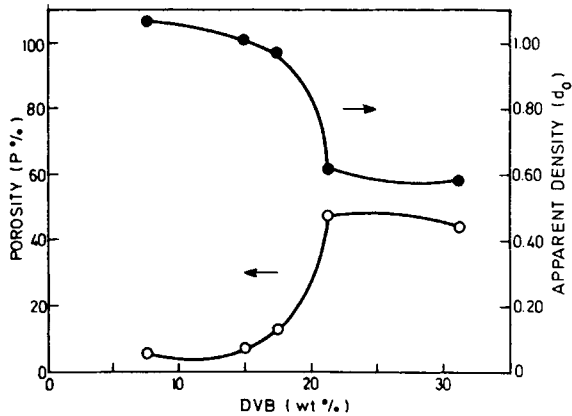


Fig. 4. Dependence of the apparent density (●) and porosity (○) on the DVB concentration: $\nu_2^0 = 0.52$.

increasing content of DVB from 18 to 22 wt % the copolymer structure changes drastically, which indicates the formation of heterogeneity prior to gelation. Figure 5 shows the syneresis by the copolymer precipitation given by the dependence of ν_2 on DVB concentration. The copolymer deswells significantly with increasing DVB content from 18 wt % to 22 wt %. At 22 wt % DVB, the ν_2 value of DOP-modified copolymer reaches nearly the value of copolymer prepared without diluent at the same DVB concentration. At this point, the copolymer, which precipitated prior to gel point, will be largely unswollen and the microspheres will be solid polymers. That is the typical condition of macroporosity.

A general condition for phase separation is the equality between the maximum swelling of the network in equilibrium with the diluent or diluent-monomer mixture $1 - \nu_{2,m}$ and the instantaneous dilution of the network characterized by $1 - \nu_2^0$, i.e.,¹

$$\nu_{2,m} = \nu_2^0 \quad (4)$$

where $\nu_{2,m}$ and ν_2^0 are the volume fractions of the polymer network in the

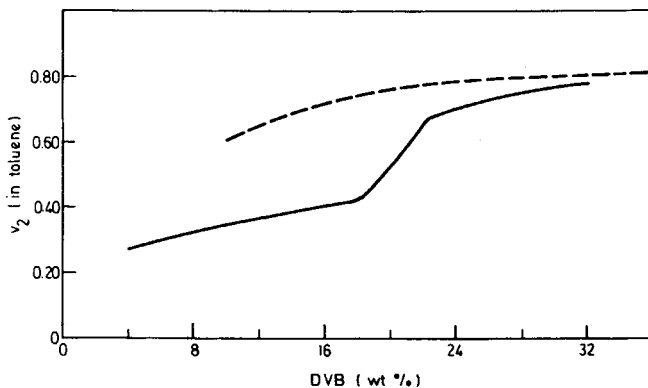


Fig. 5. Dependence of ν_2 on the DVB concentration: copolymers prepared without using diluent (---) and DOP-modified copolymers (-), $\nu_2^0 = 0.52$.

organic phase. In the presence of solvating diluents, less inhomogeneity in crosslink distribution can be expected.^{2,13} If we assume a homogeneous distribution of crosslinks, the critical value of ν_2^0/ν_{2m} remains conversion independent. Thus, if α is the volume conversion, at $\alpha = 1$, ν_2^0 reduces to ν_2^{00} and ν_{2m} may be replaced by the experimental value ν_2 , since the interaction parameter χ for copolymer-toluene is equal to those for copolymer-styrene (0.46 at 25°C), and independent of both temperature and concentration. (DOP as a plasticizer does not have much effect on the value of ν_2 .)

Thus, the condition for polymer precipitation prior to gelation reduces to $\nu_2^{00}/\nu_2 = 1$. This new relationship provides good agreement with experimental results, as shown in Figure 6. It seems that the drop in the value of ν_2^{00}/ν_2 below unity occurs between 18 and 22 wt % DVB at $\nu_2^{00} = 0.52$.

The pore size distribution of copolymers prepared with the same amount of DOP, but different amounts of DVB is given in Figure 7. It can be seen that the distribution curves are rather similar to those in Figure 3. With an increasing amount of DVB, the amount of pores about 100–500 Å in diameter increases, and they account for a considerable part of the porosity; 100–500 Å corresponds to the interstices between the microspheres in the aggregates.

The sudden change in the amount of pores (200–500 Å) at 22 wt % DVB, where the phase separation prior to gelation takes place, demonstrates the formation of the nuclei in rigid state.

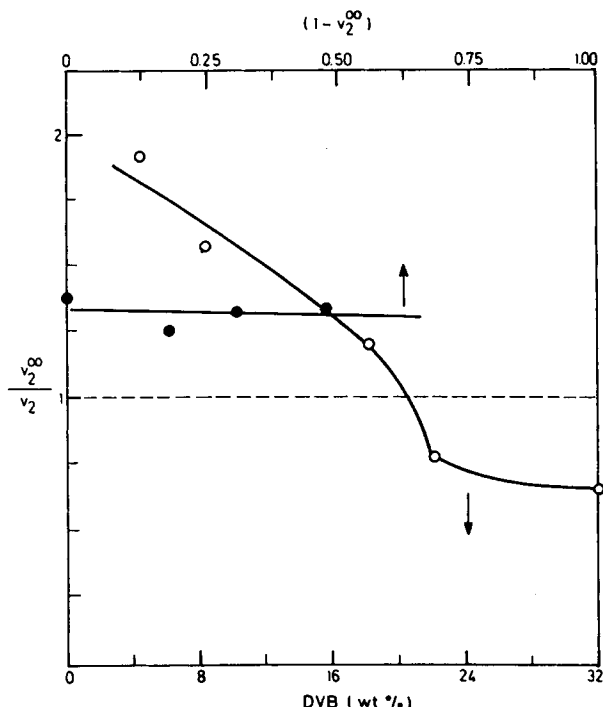


Fig. 6. Dependence of the value ν_2^{00}/ν_2 on the DOP content (●) and on the DVB concentration (○).

As shown in Figures 3 and 7, the pore size distribution of samples 1-8 is rather complex, showing a set of different size distribution. A possible reason is that if the amount of DVB is too low, the pores in the macromolecular network can collapse during the removal of the diluent or on drying, and no stable pores remain, resulting in the appearance of the individualized microspheres. This causes decrease in the porosity and an increase in the randomness of the pore size distribution.¹¹ Copolymers having sufficient DVB content retain their pore volume because of the restriction of the mobility of the polymer chains. The narrower pore size distribution of samples 9 and 10 may explain the stability of the pores in these networks.

It must be pointed out that the porosity data given in this study belongs to the dry networks. The results are reproducible when the synthesis conditions are held constant. Only inefficient mechanical conduction of pressure pulses within the porosimeter may result in negligible shifts in average pore diameter values.

CONCLUSIONS

The styrene-DVB copolymer prepared by suspension polymerization in the above-described conditions without using diluent is heterogeneous, showing that phase separation exists in the polymerization system. The

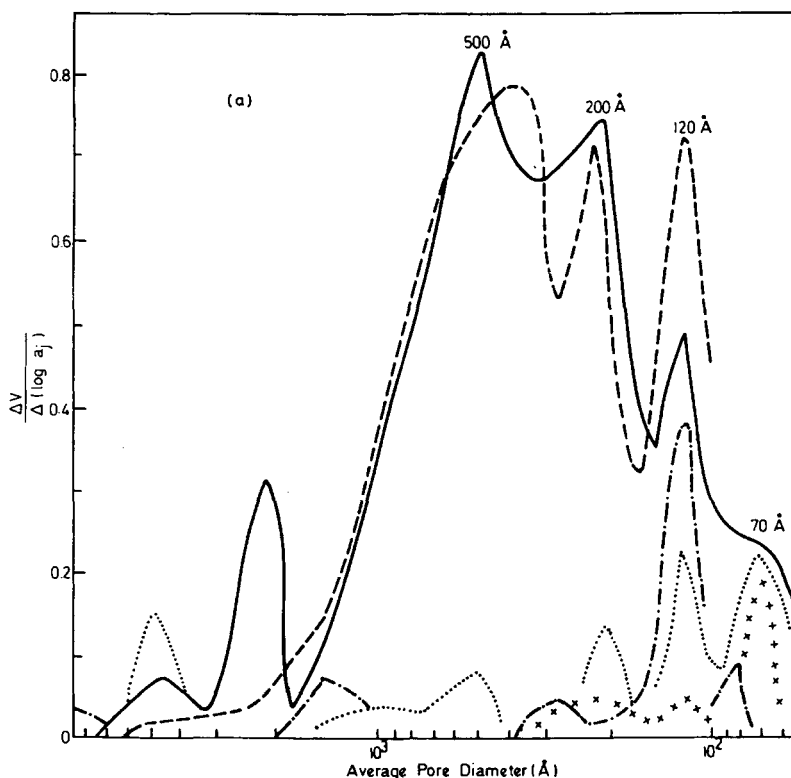


Fig. 7. Pore size distribution of copolymers prepared with various amounts of DVB in differential (a) and in integral mode (b); v_2^0 : 0.52; DVB: 8 wt % (x); 15 wt % (-.-); 18 wt % (· · ·); 22 wt % (-); 32 wt % (- - -).

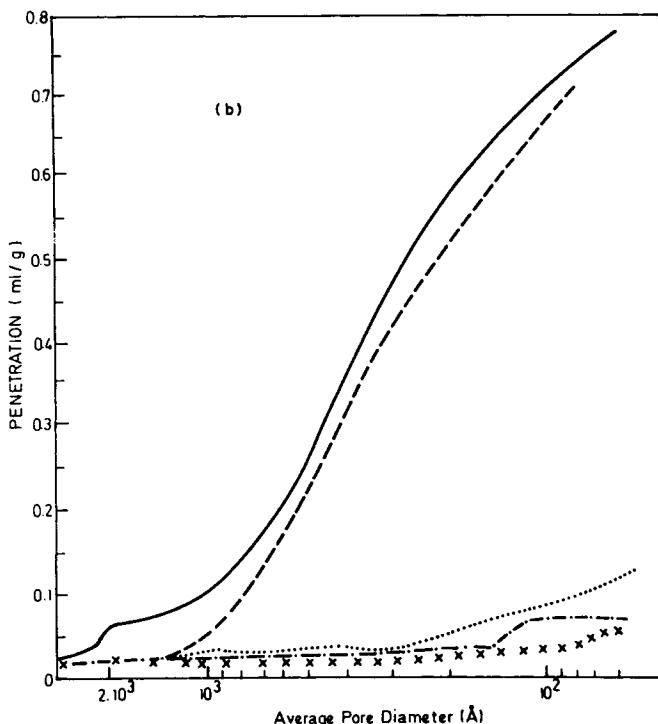


Fig. 7. (Continued from the previous page.)

addition of DOP promotes phase separation of copolymers, and increase in DVB content causes the process of phase separation to take place prior to gelation. These results were observed by the measurements of the apparent density, porosity, and swelling ratio. Assuming a homogeneous distribution of crosslinks, the experimental results were confirmed by the relationship $\nu_2^{00}/\nu_2 = 1$, which was derived from the condition of phase separation. The behavior of DOP as diluent is similar to toluene, e.g., the heterogeneity in solution occurs in toluene at about $\nu_2^{00} = 0.5^2$, and in DOP at the same DVB content at $\nu_2^{00} = 0.52$.

The process of phase separation was accompanied by the formation of pores in the range between 70 and 500 Å. The amount of these pores increases drastically by transition from homogeneous to the heterogeneous gelation. The size of these pores corresponds to the interstices of microspheres formed from the nuclei.

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