Heterogeneous Styrene–Divinylbenzene Copolymers. Stability Conditions of the Porous Structures

OĞUZ OKAY, *TUBITAK—TUGAM Research Institute for Basic Sciences, Department of Chemistry P.K. 74, Gebze, Kocaeli, Turkey*

Synopsis

The change in the porosity of styrene–divinylbenzene (S–DVB) copolymers during drying as a function of the quality of the diluent and of the divinylbenzene (DVB) concentration was investigated after drying the networks from water (maximum porosity) and from toluene (stable porosity). Two different diluents, namely toluene and cyclohexanol, were used in the polymerization system at a fixed volume fraction of the organic phase (0.50). The phase separation in toluene is accompanied by a slight deswelling of the network phase, whereas that in cyclohexanol leads to largely unswollen network phase. The stable porosity increases abruptly over a narrow range of the DVB concentration, i.e., between 40 and 50% DVB in toluene and between 15 and 25% DVB in cyclohexanol. The maximum porosity increases almost linearly with increasing DVB concentration up to a certain value, and then remains constant. The results indicate that the two main factors which determine the physical state of the swollen heterogeneous S–DVB copolymers, as well as the stability of the porous structures, are (1) the critical conversion at the incipient phase separation and (2) the degree of the inhomogeneity in crosslink distribution.

INTRODUCTION

Heterogeneous (porous) styrene–divinylbenzene (S–DVB) copolymers are widely used as starting materials for ion exchangers and as specific sorbents, and, therefore, have been the subject of a large number of studies.[1] The incipient phase separation during the S–DVB copolymerization, leading to the porous networks, can occur at a certain conversion above the gel point, resulting in the synerese of the gel, or below the gel point, resulting in the formation of a dispersion from the network and separated phases;[2,3] in both cases porous copolymers can be obtained. The porous structure of these copolymers consists of globules;[4-6] the smallest, rather spherical particles of about 100–200 Å in diameter are the "nuclei," and the aggregation of these nuclei results in the microspheres with diameters of 500–1000 Å; the microspheres are aggregated again in particles of about 2500–10,000 Å in diameter.[6] The pores are defined as the spaces between the nuclei, microspheres, and particles.

The studies on the pore structure of S–DVB copolymers are reported for samples dried under different conditions.[1,5-8] Krska et al. were the first to point out the difference in the pore structure between the swollen and the dried states.[9] Recent work has shown that the pore structure of these networks and consequently their sorption properties varies with the type of solvent used to treat the network,[10-15] and with the introduction of functional groups.[16-18] For instance, the copolymers dried from bad solvents such as

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methanol or water show a "maximum porosity",[10] which is close to the porosity in the swollen state.[13] The drying process of the copolymers swollen in good solvents such as dichloroethane or toluene may lead to a partial or total collapse of the pores. It seems that the preservation of the swollen state porosity in the dried state can be attained by decreasing the interactions between polymer chains and the solvent before the drying process, i.e., during the treatment of swollen copolymers with solvents with decreasing solvating power.

Recently, we have shown that the occurrence of the phase separation before or after gelation plays a decisive role in the pore stability of the final S–DVB networks.[18,19] It was also found that, during the drying process of the copolymers, the pores collapse in the rubbery rather than in the glassy state.[18] Furthermore, Galina and co-workers have demonstrated that the porous structure of highly crosslinked S–DVB copolymers (with 50% DVB) also changes during the drying due to the inhomogeneity in crosslink distribution.[15] In the present study, two different solvents, namely toluene and cyclohexanol, were used as the diluents in the polymerization system. For such systems, a number of studies have been reported,[1,8,20] but we shall focus here on the change of the porous structure in the post-treatment stage, in relation to the quality of the diluent and the DVB concentration. Toluene is a good solvent for polystyrene and its thermodynamic properties are the same as the monomers used in the polymerization. In addition, the polymer–solvent interaction parameter χ for the polystyrene–toluene system is independent of temperature and exhibits a weaker concentration dependence.[21] Cyclohexanol has the solubility parameter value of 11.4 (cal cm^{-3})$^{0.5}$ in contrast to the value of 9.1 (cal cm^{-3})$^{0.5}$ for polystyrene,[22] which indicates that cyclohexanol is a nonsolvating diluent for the S–DVB polymerization system.

This article describes the conditions of the pore stability of S–DVB copolymers, and discusses their morphological changes on drying. The changes in the porous structure were observed after drying of the samples from water at room temperature and from toluene at 70°C.

EXPERIMENTAL

Materials

All monomers and reagents were purified and distilled prior to use. Various batches of DVB solution were used, each with a known content of DVB isomers. Batch analyses (GC) ranged between 60 and 75% DVB isomers (m-DVB : p-DVB ratio 2–2.5 : 1), the rest being ethylvinyl benzene and nonpolymerizable compounds ($< 2\%$).

The S–DVB copolymer beads were obtained by the suspension polymerization method, as described previously.[19] The volume fraction of the monomers in the organic phase, ν_2^{00}, was taken to be constant at 0.50 throughout the study, and only the DVB concentration was varied in a wide range. 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. For comparison, part of the samples swollen in toluene was dried, without the solvent exchange, *in vacuo* at 70°C.

Porosity

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method.[23] Porosity, $P\%$, was calculated from d_0 as

$$P\% = (1 - d_0/d_2) \times 100\% \qquad (1)$$

where d_2 is the density of homogeneous S–DVB copolymers taken as 1080 kg/m^3 (Table I). The percentage of the unstable porosity, $(\Delta P/P)\%$, was

TABLE I
Composition and Properties of Copolymers[a]

Series	DVB (wt %)	$d_0 \times 10^{-3}$ (kg/m^3)		$P\%$		$(\Delta P/P)\%$	q_w	ν_2	$(\nu_2)_{\text{calcd}}$
		T	W	T	W				
I	4.4	1.08	1.08	0	0	0	1.88	0.47	—
	7.1						1.80	0.50	—
	11.8						1.39	0.67	—
	14.8						1.32	0.71	—
	25.2						1.25	0.76	—
	33.6						1.19	0.81	—
	47.6						1.18	0.82	—
II	5.1						2.47	0.35	0.31
	8.2						2.25	0.39	0.34
	14.0						2.24	0.39	0.38
	17.9	1.06	1.06	2	2	0	2.49	0.36	0.40
	22.2	1.05	1.05	3	3	0	2.34	0.38	0.41
	25.3	1.06	0.98	2	9	78	2.24	0.43	0.45
	32.6	1.01	0.99	6.5	8	19	2.31	0.41	0.45
	41.4	1.03	0.96	5	11	55	2.64	0.37	0.46
	50.6	0.82	0.75	24	31	23	2.29	0.55	0.60
	59.0	0.75	0.72	31	33	6	2.24	0.59	0.62
	66.5	0.81	0.81	25	25	0	—	—	0.55
III	2.5	1.01	1.00	7	6	13	3.3	0.28	—
	6.2	1.03	0.84	5	22	79	2.4	0.47	0.41
	12.3	1.03	0.72	5	33	86	2.31	0.57	0.56
	14.8	0.99	0.58	8	46	82	2.22	0.73	0.72
	16.0	0.91	0.55	16	49	68	—	—	0.76
	21.0	0.66	0.57	39	47	17	2.05	0.81	0.75
	24.7	0.57	0.54	47	50	6	1.19	0.83	0.80
	30.9	0.53	0.54	51	50	0	1.18	0.84	0.81

[a] d_0 = apparent density and $P\%$ = total porosity of copolymers dried from toluene (T) and from water (W), $(\Delta P/P)\%$ = the percentage of the unstable porosity, q_w = weight swelling ratio, ν_2 = volume fraction of copolymer in the swollen gel, $(\nu_2)_{\text{calcd}}$ = calculated ν_2 value using the Millar equation. The copolymers in series I were prepared without using a diluent, in series II with toluene, and in series III with cyclohexanol as the diluents.

calculated as

$$(\Delta P/P)\% = \frac{(P - P')}{P} \times 100\% \tag{2}$$

where P and P' are the porosities of samples dried from water (maximum porosity) and from toluene (stable porosity), respectively.

Swelling

The weight swelling ratio in toluene, q_w, was determined by the centrifugation method.[24] The volume swelling ratio q_v and the volume fraction of copolymer in the swollen gel, ν_2, were calculated from q_w using the equations[25]

$$q_v = \frac{d_0}{d_{2,r}} + \frac{(q_w - 1)d_0}{d_1} \tag{3}$$

$$\nu_2 = \frac{d_2}{d_{2,r}q_v} \tag{4}$$

where d_1 and $d_{2,r}$ are the densities of the solvent and the copolymer in the rubbery state, respectively ($d_1 = 867\ \mathrm{kg/m^3}$, $d_{2,r} = 1090\ \mathrm{kg/m^3}$). For comparison, the swelling value of modified copolymers was theoretically calculated using the Millar equation[20]

$$U = U_0 + D \tag{5}$$

where U is the equilibrium volume of the swelling agent (toluene) per unit mass of dry modified copolymer, i.e.,

$$U = \frac{q_w - 1}{d_1} \tag{5'}$$

U_0 is the corresponding value for homogeneous (standard) copolymers and D is the volume of the diluent per unit mass of the monomers (for $\nu_2^{00} = 0.50$; $D = 1.10$ mL/g). By using eqs. (3)–(5), the following equation for ν_2 of modified copolymers is obtained:

$$(\nu_2)_{\mathrm{calcd}} = \frac{d_2}{d_0(1 + Ud_{2,r})} \tag{6}$$

The composition of some of the prepared copolymers and their properties are given in Table I. For calculation of q_v and ν_2, the d_0 values of copolymers dried from water were used throughout the study.[18]

RESULTS AND DISCUSSION

Network Formation in Toluene

The dependence of the apparent density of toluene-modified copolymers on the DVB concentration is given in Figure 1. The apparent density does not change up to 25% DVB, which indicates that little or no shrinkage occurs in this region during the polymerization and the polymer chains are fully solvated. The lower d_0 value at 25% DVB is an indication of a phase separation in the polymerization system. The extent of the phase separation increases with further increase in the DVB concentration up to 50–60%. Moreover, the structure of copolymers up to 40% DVB shrinks on drying in the swollen state, and the pores largely disappear. From 40 to 50% DVB, the amount of stable porosity increases drastically and reaches approximately to the value of the maximum porosity (Fig. 1 and Table I).

The percentage of the unstable porosity in these networks is plotted against the degree of swelling expressed in terms of ν_2/ν_2^{00} in Figure 2 . Based on a homogeneous distribution of crosslinks, the condition for a phase separation prior to gelation is given by[19] $\nu_2/\nu_2^{00} \geq 1$. Figure 2 indicates that the amount of unstable pores increases drastically at a value of ν_2/ν_2^{00} near to unity, and then it decreases abruptly with a further increase in the ν_2/ν_2^{00} value. These suggest that the polymer chains separated after the gel point induce a loose pore structure, which can collapse on drying in the swollen state. However, the pore structure induced by a phase separation before gelation does not collapse on drying. The critical concentration of DVB at $\nu_2/\nu_2^{00} = 1$ lies between 40 and 50%.

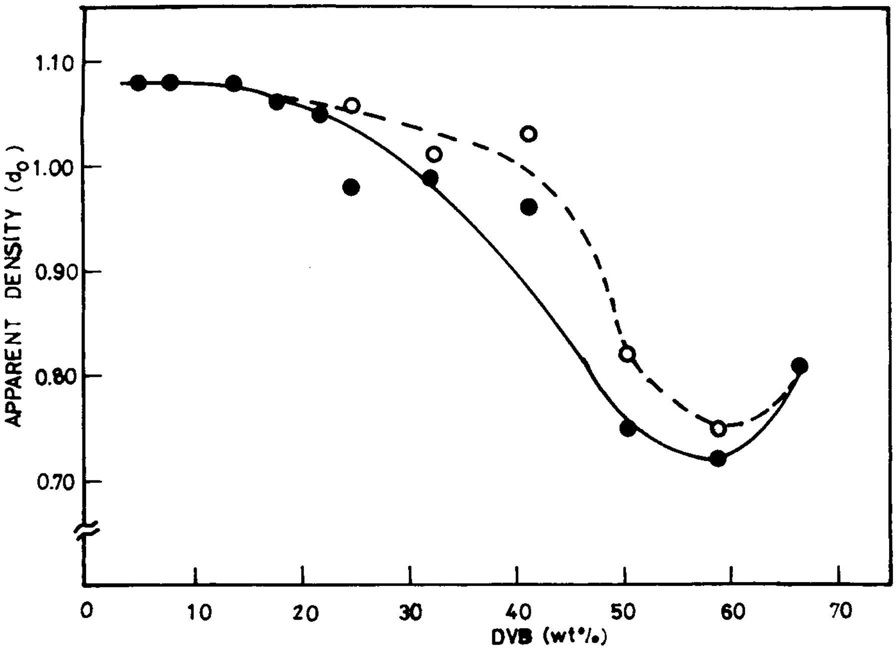

Fig. 1. Dependence of the apparent density on the DVB concentration for toluene-modified copolymers dried from water (●) and from toluene (○); $\nu_2^{00} = 0.50$.

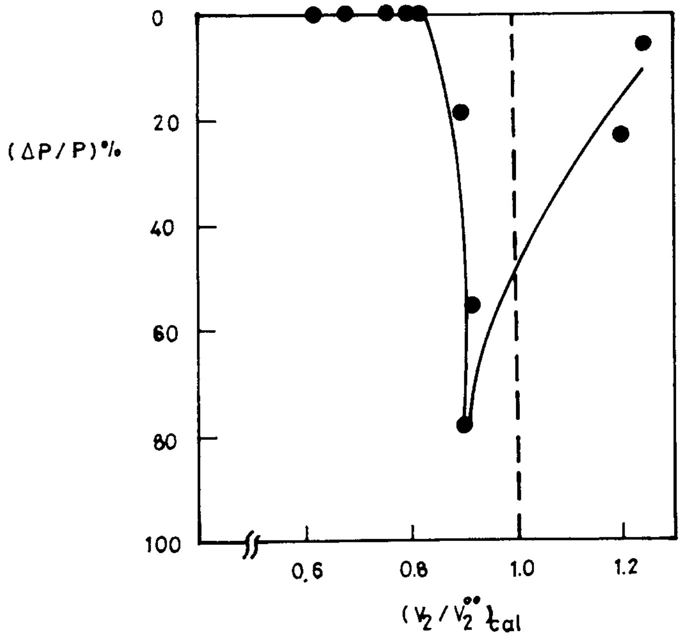

Fig. 2. Dependence of the percentage of the unstable porosity, $(\Delta P/P)\%$, on the value $(\nu_2/\nu_2^{00})_{\text{calcd}}$ for toluene-modified copolymers at $\nu_2^{00} = 0.50$.

Network Formation in Cyclohexanol

In contrast to toluene-modified copolymers, cyclohexanol induces a heterogeneous structure even at a very low degree of crosslinking due to the polymer–diluent incompatibility in the polymerization system, as shown in Figure 3. The maximum porosity of these copolymers increases linearly with the DVB concentration up to 15%, and then remains constant. Furthermore, the structure of copolymers up to 15% DVB shrinks on drying, whereas, over a narrow range in the DVB concentration between 15 and 25%, the stability of the pores increases abruptly.

The extent of the pores' collapse is plotted against the swelling value in Figure 4 which shows that the changes in porosity on drying occur in a wide range of ν_2. It is expected that the unfavorable reaction medium in this system leads to a phase separation very early and prior to the gel point, almost independent on the DVB concentration. This heterogeneity may result in a very broad distribution of chain lengths between crosslinks.[3] In such highly inhomogeneous copolymers, the time of the phase separation during the network formation seems to be insufficient to explain the porosity changes during drying.

Figure 5 shows the experimentally determined ν_2 values for three series of copolymers plotted against the DVB concentration. The solid curve illustrate the experimental ν_2 vs. DVB% for homogeneous copolymers in series I (cf. Table I). The dotted curves were calculated for modified copolymers using eq. (6) and are in good agreement with the experimental data points (Fig. 5 and Table I). The heavy line in Figure 5 represents the critical ν_2 values for glassy

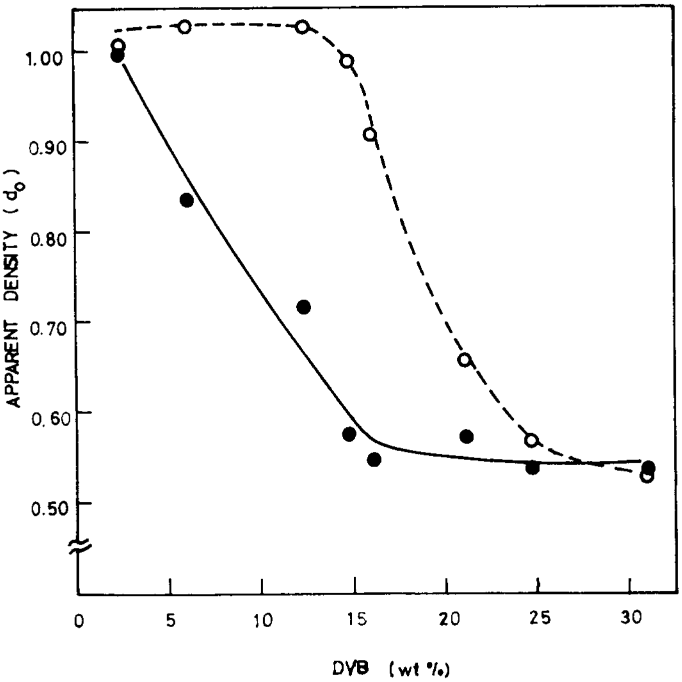

Fig. 3. Dependence of the apparent density on the DVB concentration for cyclohexanol-modified copolymers dried from water (●) and from toluene (○); $\nu_2^{00} = 0.50$.

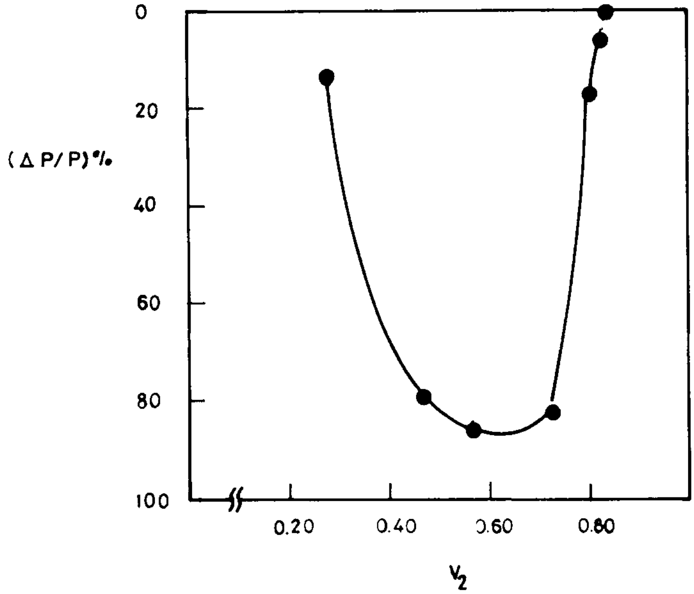

Fig. 4. Dependence of the percentage of the unstable porosity, $(\Delta P/P)\%$, on ν_2 of cyclohexanol-modified copolymers at $\nu_2^{00} = 0.50$.

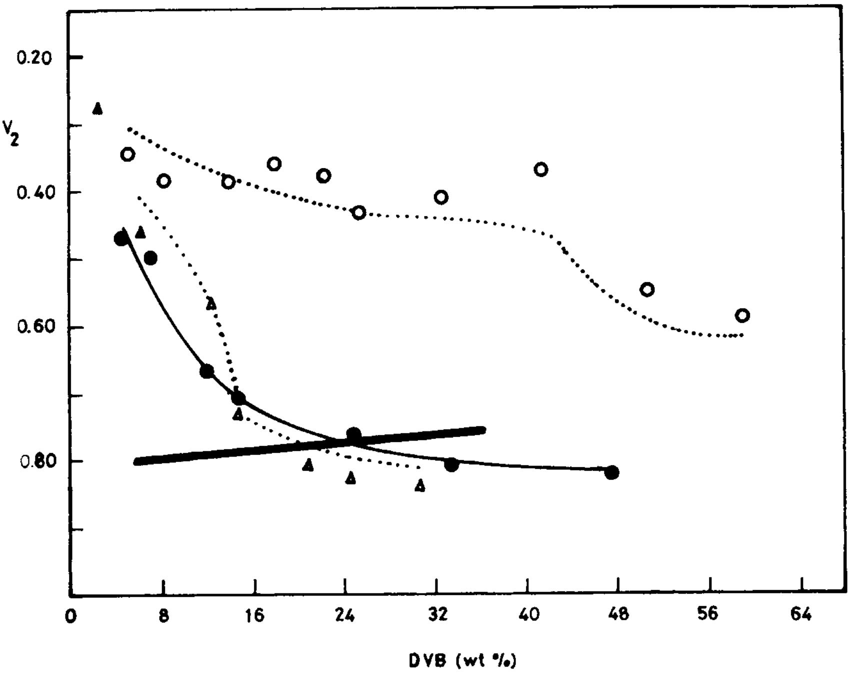

Fig. 5. Dependence of ν_2 on the DVB concentration: (●) copolymers prepared without using diluent; (○) toluene-modified copolymers; (△) cyclohexanol-modified copolymers; (· · ·) calculated using the Millar equation;[18] (——) critical ν_2 values for glassy transition of copolymers swollen in toluene at room temperature (293 K).

transition of copolymers swollen in toluene at room temperature, calculated as in Ref. 18; the copolymer gels in toluene are in the glassy state below this line.

The phase separation in the presence of toluene seems to be accompanied by a slight deswelling of the network phase. In the case of cyclohexanol as the diluent, the separated network phase is largely unswollen, and at 15% DVB, the final network swells in the same amount as the homogeneous network at the same DVB concentration. With a further increase in the DVB concentration, the modified copolymer swells less than the corresponding homogeneous copolymer due to the "inverse synerese"[1,2] in the polymerization system.

The phase separation prior to the gel point leads to an abrupt increase in ν_2, which results in the copolymer gel remaining in the glassy state during the swelling, and thus in an increase in the stability of the pores. As seen from Figure 5, the homogeneous copolymers swollen in toluene with a DVB content below 24%, or with a ν_2 value below 0.78, are in the rubbery state. Therefore, the pore structure of a heterogeneous network with $\nu_2 < 0.78$ cannot be stable, even if the pore structure has formed in heterogeneous gelation. Therefore, the amount of the stable porosity in cyclohexanol-modified samples reaches a maximum value at $\nu_2 \cong 0.80$, corresponding to a DVB content between 20 and 25% (Fig. 4).

The parts formed later in such highly inhomogeneous networks, i.e., the surface of the aggregates, can collapse on drying, since these regions will have lower crosslink density than those of the inner part of the aggregates[15,26] and will pass locally in the rubbery state on swelling. The partial collapse of the pores in samples with 20–25% DVB must be due to the weaker crosslinked regions in this network. Conversely, stable pores exist in copolymers with a DVB content lower than 20% due to the highly crosslinked regions (Fig. 3 and Table I).

CONCLUSIONS

Two main factors determine the physical state of swollen heterogeneous S–DVB copolymers, and therefore the stability of the pores:

1. The time position of the phase separation and gelation during the course of the polymerization.
2. The degree of the inhomogeneity in crosslink distribution of the copolymers.

The process of phase separation prior to the gel point is accompanied by an abrupt increase in ν_2 of the final networks. The increase in ν_2 results in an increase in the glass transition temperature of polymer–solvent system, so that the system may remain in the glassy state during the swelling resulting in an increase in the stability of the pores. However, if the DVB concentration is not sufficiently high, the pores induced by a phase separation prior to the gel point can collapse on drying.

The inhomogeneity in crosslink distribution due to the different reactivities of the monomers[27] also plays an important role in the pore stability of the final copolymers. During the polymerization, the more reactive monomer, DVB, is exhausted more rapidly than the styrene. Accordingly, the earlier phase separated portions of the network with higher crosslink density (inner part of the aggregates) do not collapse, whereas those with lower crosslink density (surface of the aggregates) can collapse on drying. In the presence of a poor solvent such as cyclohexanol as the diluent, highly inhomogeneous copolymers are obtained. Therefore, the extent of changes in the porosity during drying increases in such networks.

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