Formation and Structural Characteristics of Porous Ethylene Glycol Dimethacrylate Networks

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SYNOPSIS

The relationships between the synthesis conditions and the morphology of ethylene glycol dimethacrylate (EGDM) networks were investigated. EGDM networks were prepared by free-radical polymerization in toluene as a diluent. The networks were characterized by swelling, porosity, and pendant vinyl group content measurements. The accessibility of pendant vinyls to low molecular weight compounds was tested using pyrrolidine as a model reactant. The results show that the polymerization of EGDM in toluene is accompanied by a phase separation in the system. The networks thus obtained are heterogeneous and exhibit an inhomogeneity in the porosity and swelling distributions. Both the weight swelling ratio and the pore volume of the networks increase with increasing monomer dilution. It was also found that the accessibility of pendant vinyls increases as the cross-linking density of the network decreases or as its porosity increases. The results can be explained with the formation of highly cross-linked microgels as the intermediates in the network formation processes. Two equations were derived to predict the equilibrium weight swelling ratio and the pore volume of heterogeneous networks. Satisfactory agreement of the results of measurements with the predictions of the equations was observed.

INTRODUCTION

Ethylene glycol dimethacrylate (EGDM) has been widely used as a cross-linking agent in the synthesis of hydrophilic or hydrophobic copolymer networks. The most common combination from the viewpoint of application is its copolymers with glycidyl methacrylate (GMA)[1] or 2-hydroxyethyl methacrylate (HEMA).[2] For instance, GMA–EGDM copolymer networks can be used as carriers in the immobilization of enzymes. Moreover, their epoxy groups also offer a possibility to obtain various functional groups by additional modifications.[3,4]

A drawback of using such carriers is that only a small fraction of functional groups is accessible for the active sites of enzymes or reagents in the aqueous media. Our research has shown that, even in highly porous GMA–EGDM networks, only 1–3 mol % of the epoxy groups are accessible to the thiosulfate anions, as determined by the thiosulfate method.[5] This poor performance of GMA–EGDM networks probably originates from the steric hindrance of the cross-linked structure as well as from the hydrophobic nature of the networks. To overcome this, a delayed charge of functional monomers to the partially prepolymerized EGDM was suggested.[6]

Our attention has been directed to the polymerization of EGDM alone, due to the fact that, after the reaction was complete, various amounts of pendant vinyl groups remained in the network structure. These vinyls may be subsequently copolymerized with functional monomers yielding reactive surfaces or star-shaped macrogels. In this case, however, the reactivity of pendant vinyls is important, which, in turn, depends on the morphology of EGDM gel particles.

The objective of this study is to investigate the relationships between the synthesis conditions and the morphology of EGDM networks. For this purpose, a number of EGDM networks were prepared by free-radical polymerization. Toluene was used as the diluent in the polymerization system. The effect

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of the polymerization parameters such as the reaction time and the EGDM concentration on the network properties was studied using measurements of swelling, porosity, and pendant vinyl group content of the networks. The accessibility of pendant vinyls in the network structure was tested using pyrrolidine as a model reactant.

As is well known, monovinyl–divinyl monomer copolymerization cross-linking reactions in the presence of a diluent lead to the formation of expanded (preswollen) or porous structures, depending on the synthesis conditions.[7] Porous structures are obtained as a result of a phase separation during the polymerization process. Many studies have been reported in the literature on the synthesis–property relations of porous networks, especially those of styrene–divinylbenzene copolymers.[7-19] It is also a well known fact that the porosity of the networks increases as the concentration of the divinyl monomer or the diluent increases or as the solvating power of the diluent decreases. However, there is no quantitative correlation available to predict the characteristics of the networks, such as swelling, porosity, pore size, and pore-size distribution, from their synthesis conditions. In this paper, we also attempt to derive general porosity–swelling–dilution relations from the experimental data to provide greater insight into the phenomenon of network formation processes.

EXPERIMENTAL

Materials

EGDM (Merck) was freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing, and drying over sodium sulfate. It was then distilled under reduced pressure over copper(I) chloride as a polymerization inhibitor. The GC analysis of EGDM gave the following results: 98% EGDM and 1% HEMA. The initiator, 2,2′-azobisisobutyronitrile (AIBN, Merck) was recrystallized from methanol. Toluene (Merck) was used as received (> 99% purity).

Polymerization

The radical polymerization of EGDM was performed at 80°C in bulk or in toluene solution. AIBN as an initiator (0.43 wt % of the monomer) was dissolved in the selected monomer–toluene mixture, and this was divided and transferred into a series of glass tubes of 5 mm internal diameter and about 250 mm long. The glass tubes were degassed, sealed under vacuum, and placed in a thermostat at 80 ± 0.5°C for a predetermined polymerization time. The reactions were stopped by cooling the tubes with liquid nitrogen. Homologous series of EGDM networks were prepared in this way, allowing systematic variation of the EGDM concentration and the reaction time.

Extraction of the Sol Fraction

Toluene was chosen as the extraction solvent and employed at room temperature. The crude gels were cut into samples of 10–25 mm length. To remove the sol fraction, each sample was placed in an excess of toluene containing a small amount of 1,4-benzoquinone as an inhibitor. After 5 days with occasional shaking, benzoquinone-containing toluene was replaced with pure toluene and the extraction was continued for 1 day further. The networks after extraction were carefully deswollen in a series of toluene–methanol mixtures with increasing methanol contents. They were then washed with methanol and dried at room temperature under vacuum to constant weight.

The gel conversion was calculated as the ratio of the weight of the extracted network to that of the initial monomer.

Methods

The apparent density of the networks, d_0, was determined by the mercury pycnometric method. Porosity, $P\%$, and pore volume, V_p, were calculated from d_0 as

$$P\% = \left(1 - \frac{d_0}{d_2}\right) \times 100\% \tag{1}$$

$$V_p = \frac{1}{d_0} - \frac{1}{d_2} \tag{2}$$

where d_2 is the homogeneous polymer density, taken as 1.20 g/cm^3 (Table II). Here, $P\%$ and V_p represent the total volume of pores in 100 mL or in 1 g of dry polymer, respectively.

The swelling measurements were carried out in toluene at room temperature. To reach the equilibrium degree of swelling, the networks were immersed in toluene for at least 1 week; the swelling equilibrium was tested by weighing the samples. To achieve good precision, four measurements were carried out on samples of different weight taken from the same gel. The networks were then weighed in the swollen state and dried under vacuum to constant weight.

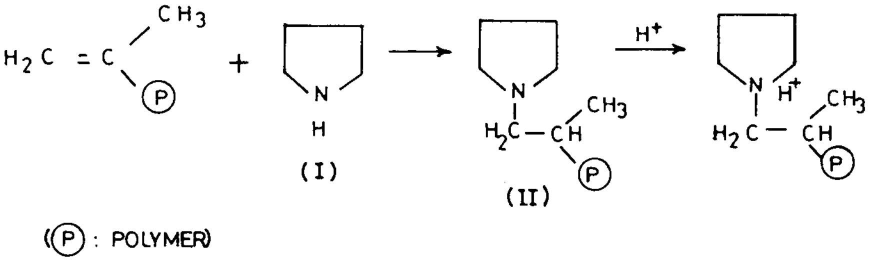
The weight swelling ratio, q_w, was calculated using the equation

$$q_w = w_s / w_d \tag{3}$$

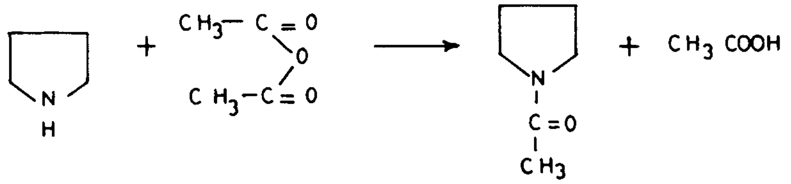
where w_s and w_d are the swollen and initial weights of the polymer, respectively.

Pendant Vinyl Groups

The pendant vinyl groups in the polymer accessible to low molecular weight reactants were determined using the pyrrolidine method.[20,21] The method is based on the reaction of vinyl groups with pyrrolidine (**I**), and titration of the formed tert-amine (**II**) with a standard acid solution:



Prior to the acid titration, the excess of pyrrolidine is deactivated using acetic acid anhydride:



In the present study, the original method was modified by taking toluene instead of benzene as the solvent in order to increase the reaction temperature. Preliminary experiments showed that the vinyl groups in the EGDM monomer react quantitatively with pyrrolidine after a reaction time of 2 h. For the gel samples, the reaction time was increased to 6 h. The following procedure was applied throughout this study:

About 150 mg of the polymer was weighed in a 100 mL flask containing a Teflon-covered magnetic stirring bar. To this, toluene (50 mL), pyrrolidine (3 mL, Merck), and acetic acid (0.5 mL, Merck) were added and the mixture was refluxed for 6 h under stirring. The solution was then cooled to room temperature, and after addition of 6 mL of acetic acid anhydride (Merck), it was stirred for 1 h at room temperature. The mixture was then transferred into a beaker with 5 mL of methanol and titrated potentiometrically with 0.1N methanolic HCl using glass electrodes (Metrohm E 536 Potentiograph, 655 Dosimat).

The fraction of units in the polymer bearing accessible pendant vinyls, PV_a, was calculated as

$$PV_a = \frac{N \times (X - Y)}{m/M} \tag{4}$$

where N is the normality of the standard HCl solution, X and Y are its volumes consumed in the presence and absence of a polymer sample, respectively (both in mL), m is the sample weight in mg, and M is the molecular weight of the EGDM units (198 g/mol). According to eq. (4), if $PV_a = 1$, each monomeric unit in the polymer carries one accessible pendant vinyl group.

The total content of pendant vinyls in the network, PV_t, was estimated from IR spectra. The IR spectra of the networks in KBr pellets were recorded on a Perkin-Elmer 983 spectrophotometer. A typical spectrum of the EGDM networks is shown in Figure 1. The absorption peaks of unreacted vinyl groups are shown at 1640 cm^{-1} due to the $C{=}C$ stretching vibration and at 950 cm^{-1} arising from $=CH_2$ wagging vibration. The peak at 1640 cm^{-1} was influenced by traces of water. Therefore, the peak at 950 cm^{-1} was used in the calculations and it was normalized using the peak of methyl groups at 1390 cm^{-1}. The calculation of the absorbances was performed using the base-line method[22] (Fig. 1). PV_t was estimated as

$$PV_t = \frac{A_{950}}{A_{1390}} \tag{5}$$

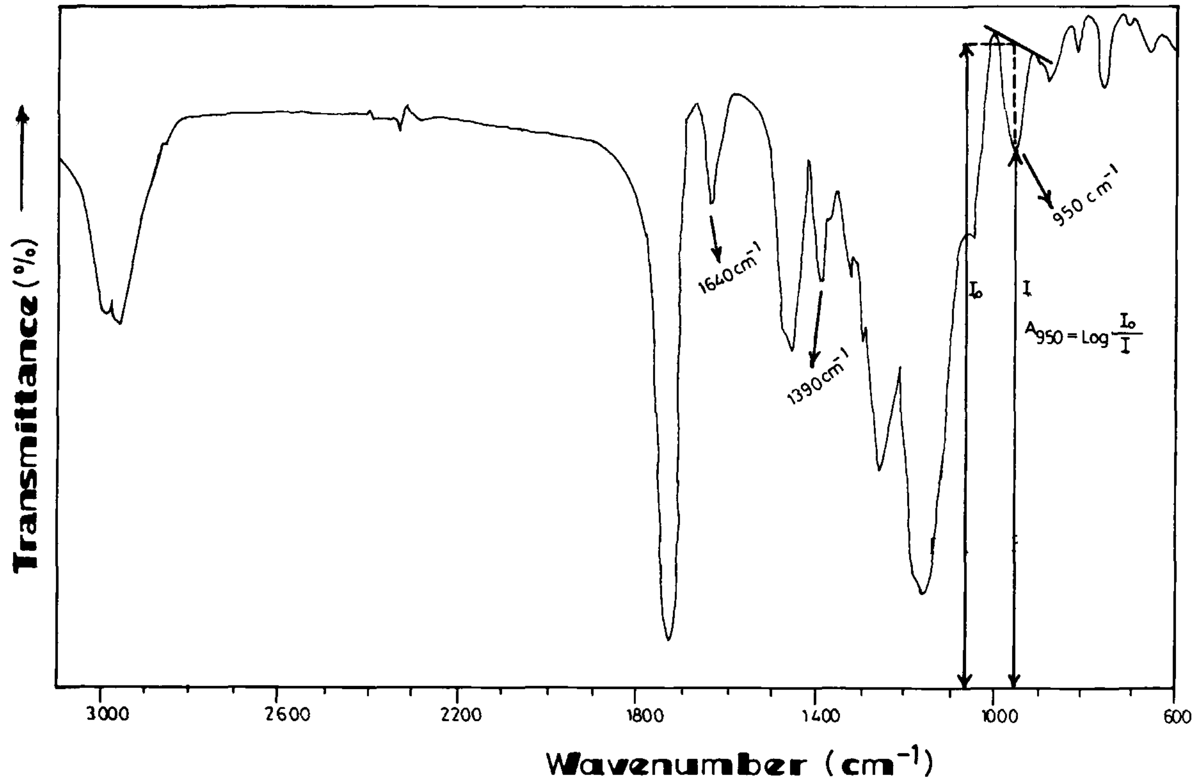


Figure 1 IR spectrum of an EGDM network in the KBr pellet. Polymerization time = 20 h. Initial monomer concentration = 50 vol %. The calculation of absorbance is shown schematically at 950 cm^{-1}.

where A_{950} and A_{1390} are the absorbances at 950 cm^{-1} and 1390 cm^{-1}, respectively.

RESULTS AND DISCUSSION

Network Formation

In the literature, very few studies deal with the EGDM polymerization. Aso investigated the course of radical EGDM polymerization and proposed a kinetic scheme of the reactions.[23] Funke and co-workers studied the anionic EGDM polymerization.[24,25] They observed the formation of intramolecularly cross-linked polymer particles with diameters smaller than 60 nm, called reactive microgels, as the intermediates of the reaction. Reactive EGDM microgels were also isolated by Galina and co-workers in the radical polymerization in benzene.[26] Fifty to seventy percent of the EGDM units in the microgels bore pendant vinyl groups.

In this section, we have attempted to investigate the properties of EGDM networks depending on the extent of the polymerization and cross-linking reactions. The polymerization was carried out at 80°C in toluene and at an initial monomer concentration 50 vol %.

Visual observation showed that the reaction mixture becomes turbid after a polymerization time of 1.5 min, indicating the occurrence of a phase separation in the system. Since EGDM–toluene mixtures are good solvents for the formed polymer, a phase separation may only occur due to the increasing cross-linking density of the polymer.[7] Accordingly, the maximum swelling of the polymer gel will decrease during the course of the EGDM polymerization until it reaches the concentration of the residual monomer–diluent mixture. At this point, as the maximum swelling cannot be smaller than the degree of dilution, the originally homogeneous system must separate into two phases, resulting in the appearance of a turbidity in the reaction mixture.

The gel conversion and the equilibrium weight swelling ratio of the EGDM networks, q_w, are shown in Figure 2 as a function of the polymerization time. In Figure 3, the time dependence of the reciprocal q_w values is given. By extrapolating the curves to zero gel conversion or to infinite swelling ($q_w^{-1} = 0$),

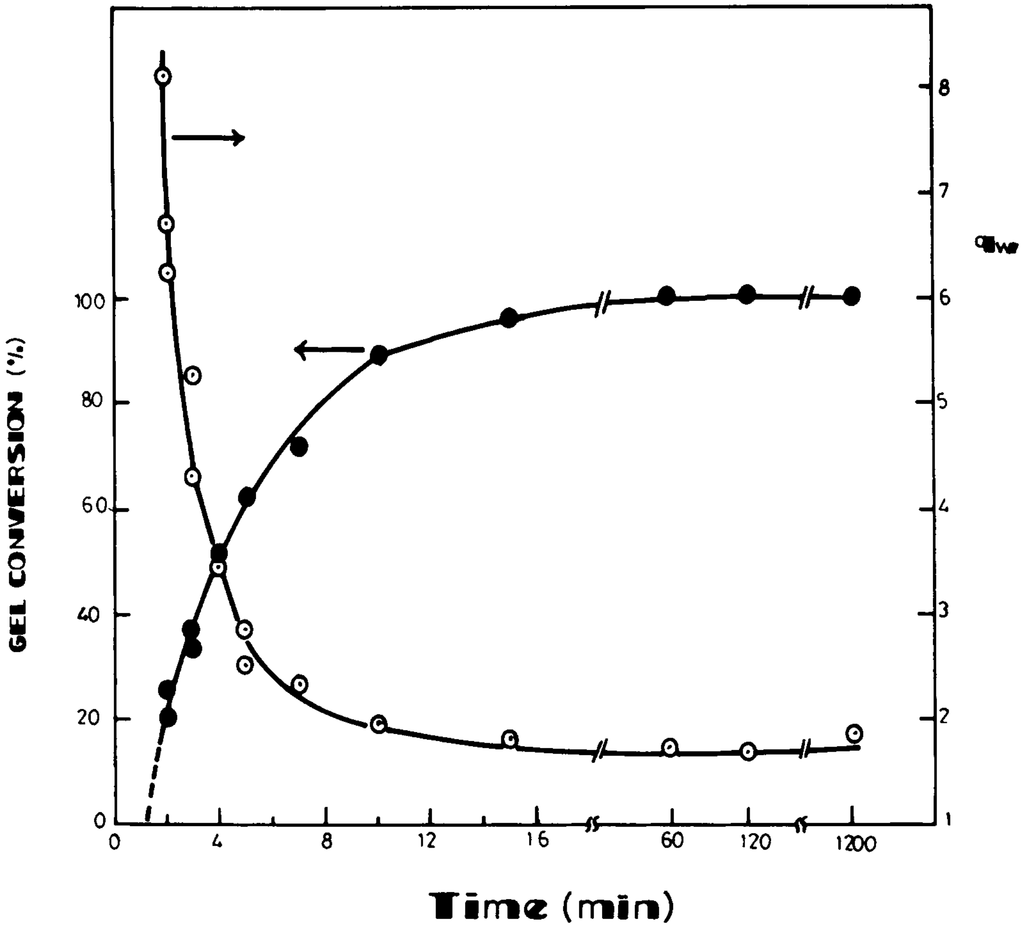


Figure 2 (●) Dependence of the gel conversion and (⊙) the equilibrium weight swelling ratio of the gel in toluene, q_w, on the polymerization time. Initial monomer concentration = 50 vol %. Polymerization temperature = 80°C.

we obtain a reaction time of about 1.4 min for the onset of gelation. Comparing this with the time needed for the appearance of a turbidity (1.5 min), we can conclude that the incipient phase separation in the reaction mixture takes place as soon as a macrogel is formed. Thereafter, the gel conversion increases and the equilibrium swelling of the gel decreases rapidly as the reaction proceeds and they reach limiting values after similar times (Fig. 2). The high rates of the polymerization and crosslinking reactions in the EGDM polymerization may be a consequence of autoacceleration due to the gel effect of the viscous reaction medium.

Figure 4 shows the apparent densities of the networks, d_0, plotted against the polymerization time. d_0 decreases abruptly with increasing time of polymerization up to the 10th min and then remains almost constant. Visually, it was observed that the gels after synthesis consist of a white (porous) core, surrounded by a shell of transparent, relatively swollen gel. The thickness of the transparent shell decreased with increasing time of polymerization and vanished after 20 h. These results indicate an inhomogeneity in the porosity and swelling distribution in the gel samples whose extent decreases with increasing reaction time. Thus, the measured q_w and d_0 values shown in Figures 2 and 4 must be taken as the means of those of various regions.

The inhomogeneous nature of the EGDM gels can be explained as follows: Unlike the divinylbenzene isomers, the vinyl groups in EGDM have independent reactivities,[9] i.e., after one of the vinyls has reacted, the reactivity of the remaining vinyl (pendant vinyl) does not change. Therefore, intramolecularly cross-linked EGDM polymers called EGDM microgels are formed at the very beginning of the EGDM polymerization.[25,26] After the formation of the microgels, the equal reactivity condition of vinyl groups may not be valid due to steric reasons. As the reaction proceeds, the microgels are con-

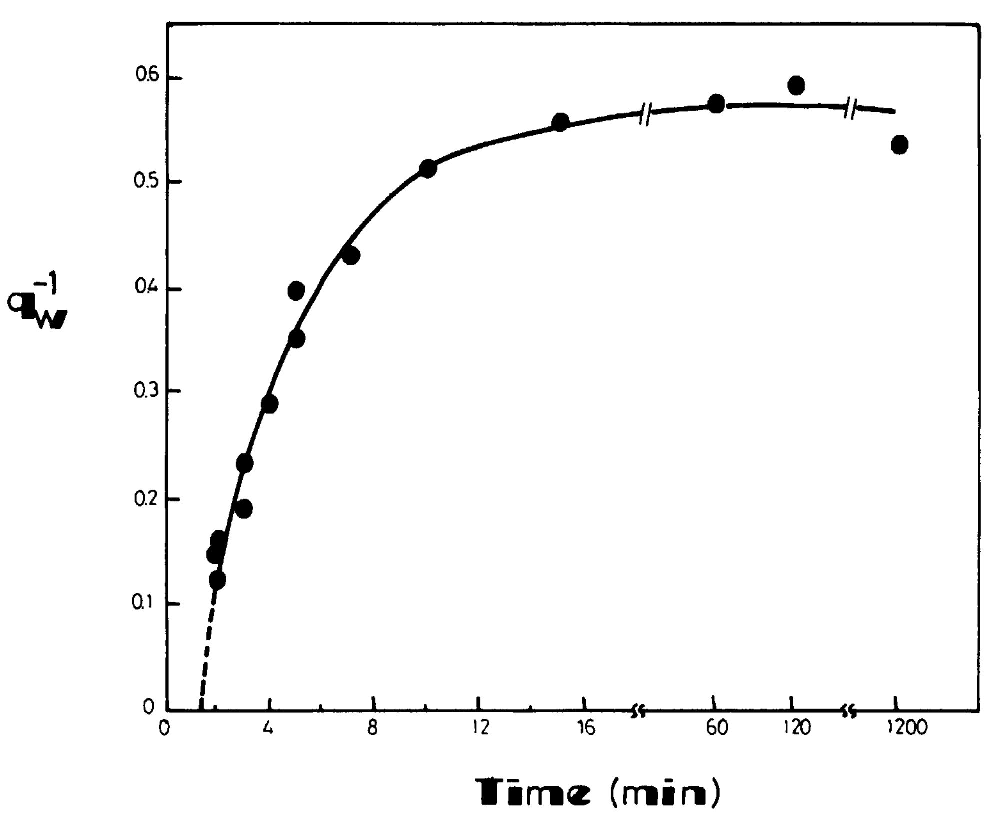


Figure 3 Dependence of q_w^{-1} on the polymerization time in the EGDM polymerization in toluene at 80°C. Initial monomer concentration = 50 vol %.

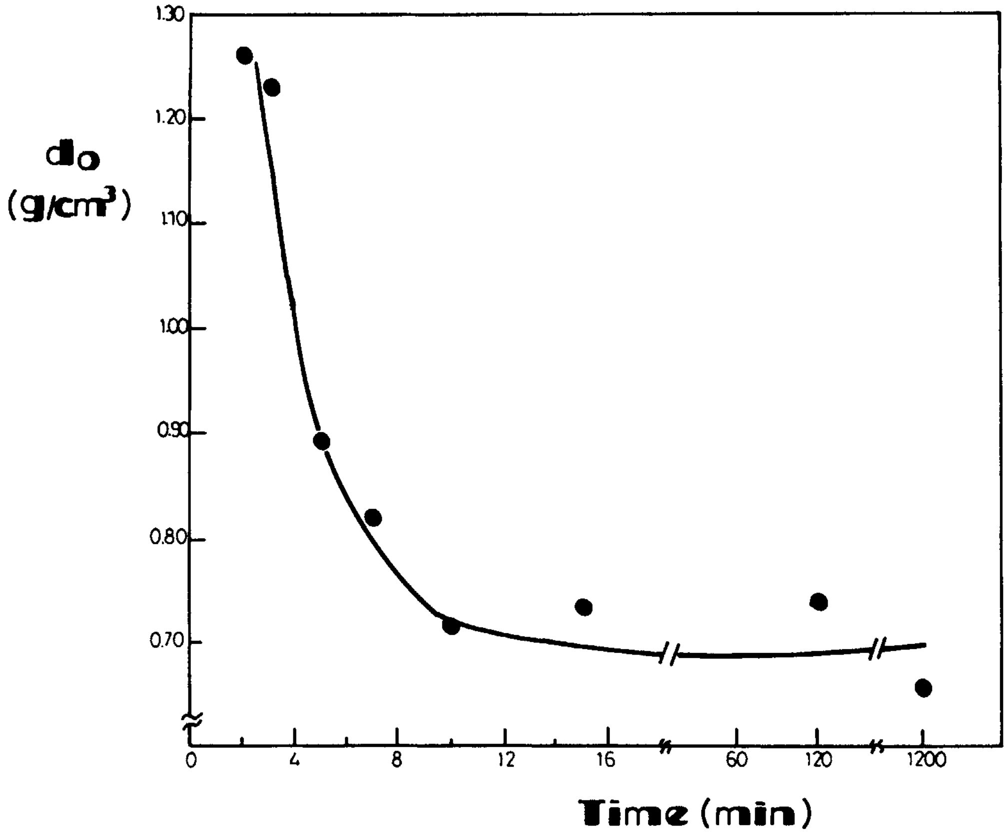


Figure 4 Dependence of the apparent density of the networks, d_0, on the polymerization time in the EGDM polymerization in toluene at 80°C. Initial monomer concentration = 50 vol %.

nected to a macrogel through their peripheral pendant vinyls and radical ends, whereas those in their interior remain intact. At the onset of the phase separation, a dilute solution phase containing EGDM, toluene, and free microgels separates out of the network phase and the network collapses. Thereafter, the reaction in the solution phase can be expected to proceed at a slower rate than that in the network phase due to the low monomer concentration as well as due to the absence of a gel effect, leading to the formation of less porous and more swellable regions in the network at insufficient reaction times.

The amount of pendant vinyls in the network accessible to low molecular weight reactants was determined using pyrrolidine as a model reactant. The solvent used for the measurements was toluene, which is a good solvent for the EGDM networks. Figure 5 shows the fraction of units in the gel bearing accessible pendant vinyls, PV_a, together with the total content of pendant vinyls, PV_t, estimated from the IR spectra of the networks, as a function of the polymerization time. After 2 min of polymerization, 40–50% of the monomeric units bear accessible pendant vinyls; but this value decreases abruptly as the reaction proceeds and reaches to a limiting value of 1% after 10 min. The total content of pendant vinyls also shows a similar dependence on the reaction time.

It was interesting to observe that the absorbances of pendant vinyls in the IR spectra decreased only slightly after the reaction of the networks with pyrrolidine. Even by the loosely cross-linked networks isolated after 2 min of polymerization, with q_w values ranging from 6.25 to 8.1, the peaks at 950 and 1640 cm^{-1} are visible after the pyrrolidine reaction (Fig. 6 and Table I). Similar trends were also observed by other networks prepared at different reaction times and for various initial monomer concentrations. In Table I, the values PV_t both before and after pyrrolidine reaction and PV_a are shown for various initial monomer concentrations and for a

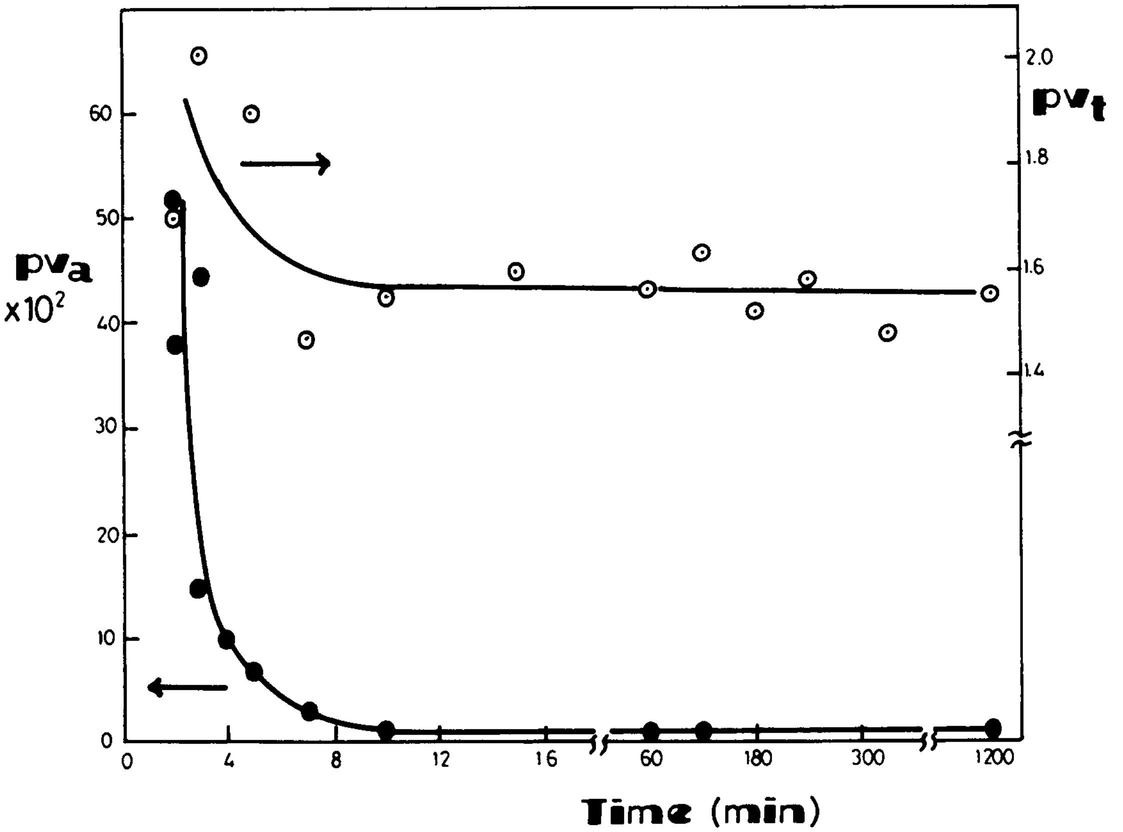


Figure 5 (●) Dependence of the fraction of units in the gel bearing accessible pendant vinyls, PV_a, and (⊙) the total content of pendant vinyls estimated from IR spectra, PV_t, on the polymerization time. Initial monomer concentration = 50 vol %. Polymerization temperature = 80°C.

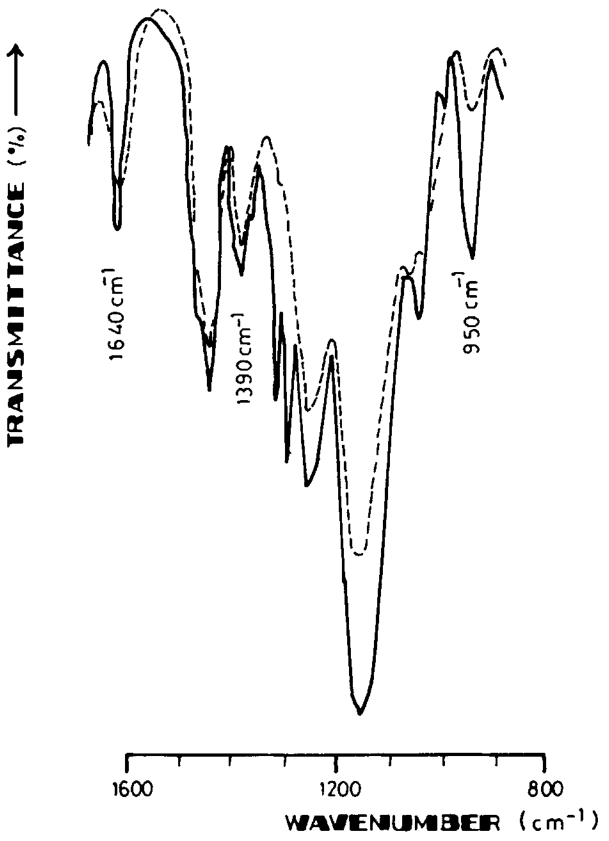


Figure 6 IR spectra of an EGDM network in the KBr pellet both before (——) and after its reaction with pyrrolidine (- - -) Initial monomer concentration = 50 vol %. Polymerization time = 2 min. Polymerization temperature = 80°C.

reaction time of 2 h. The slight decrease in PV_t after the pyrrolidine reaction indicates that only a small fraction of pendant vinyls is accessible to the reactant. It can be expected that the unreactive vinyls are located inside the microgel particles and, thus, they have no chance for reactions because of the compact, cross-linked structure of EGDM microgels. In this connection, it can also be expected that the high degree of swelling of the networks formed at low gel conversions, i.e., the loose network structure originates from the low number of bridges connecting the highly cross-linked microgels to an infinite network.

Another point shown in Table I is that as the monomer concentration decreases the number of pendant vinyls in the network decreases but their accessibility toward the model reactant increases (Fig. 7). These results are reasonable since the rate of consumption of vinyl groups during the polymerization increases with increasing dilution due to the predominant cyclization.[9] On the other hand, as we will show in the next section, the networks become more porous with increasing dilution, leading to an increase in the accessibility of pendant vinyls.

Porosity–Swelling–Dilution Relations

Series of EGDM networks were prepared in toluene at various initial monomer concentrations between 100 and 11 vol % EGDM. The polymerization time was held constant at 20 h. The synthesis conditions of the networks and their properties are collected in Table II. The monomer concentrations are expressed as the vol % commercial EGDM and also as the volume of the diluent (toluene) added per gram of the monomer (v_d). Measurements showed that the pores in all of the networks shown in Table II are stable,[27] i.e., they do not collapse on drying in the swollen state. As expected, both the equilibrium weight swelling ratio and the total porosity of the networks increase with increasing dilution. At 11.1 vol % EGDM concentration (v_d = 7.628 mL toluene/g EGDM), the network absorbs more than sevenfold of its own weight toluene and exhibits a total porosity of 84% (4.35 mL/g pore volume).

In Figure 8, the equilibrium weight swelling ratio of the networks in toluene, q_w, is shown as a function of the monomer concentration in terms of v_d (volume of the diluent added per g of the EGDM monomer). The experimental data points are shown with the filled circles. The solid line is the best fit to experimental data given by the equation

$$q_w = 1.12 + 0.81v_d \qquad (6)$$

Table I The Fraction of Units in the Gel Bearing Accessible Pendant Vinyls, PV_a, and the Total Content of Pendant Vinyls, PV_t, Both Before (1) and After Pyrrolidine Reaction (2) for Various Initial Monomer Concentrations

EGDM (Vol %)	$PV_a \times 10^2$	PV_t (1)	PV_t (2)
100.0	0.6	1.68	1.18
66.7	0.5	1.74	1.18
50.0	1.0	1.55	—
44.4	1.0	—	—
33.3	—	0.98	—
20.0	—	0.64	—
13.5	3.5	0.62	0.52
50.0[a]	38.6–52.0	1.70	0.57

Polymerization time = 20 h. Polymerization temperature = 80°C.

[a] Polymerization time = 2 min.

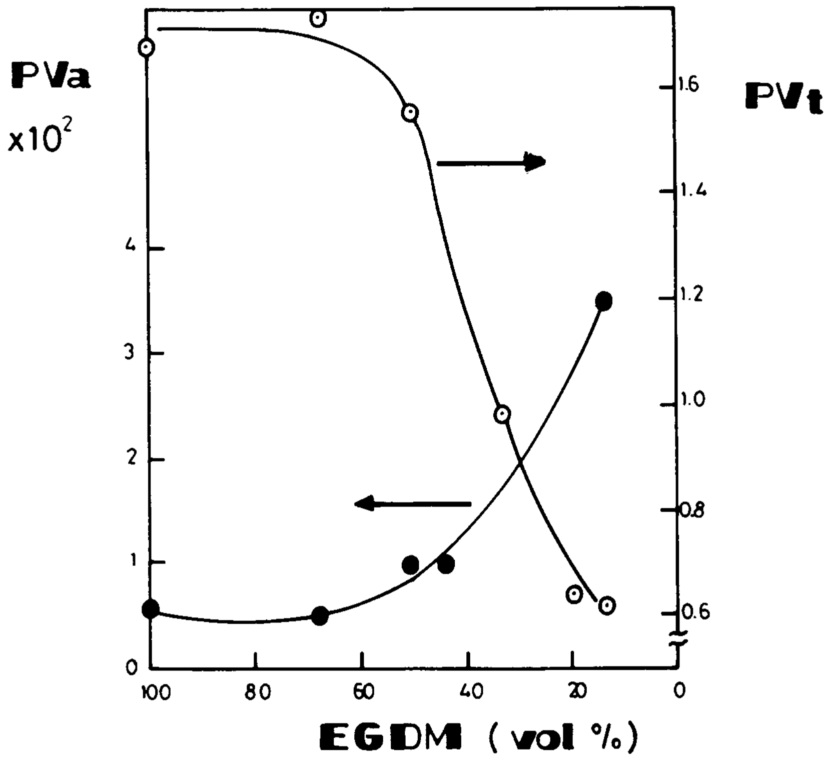


Figure 7 (●) Dependence of PV_a and (⊙) PV_t on the initial monomer concentration. Polymerization time = 20 h. Polymerization temperature = 80°C. See Figure 5 caption.

with a correlation coefficient $r = .9994$. Assuming that all the diluent (toluene) present in the starting monomer mixture remains in the network after synthesis, the weight swelling ratio of extracted networks can be calculated as

$$q_w = q_{w,0} + d_1 v_d \qquad (7)$$

where $q_{w,0}$ is the value q_w of the network prepared without using a diluent and d_1 is the density of the swelling agent. The dashed line in Figure 8 was cal-

Table II Synthesis Conditions and Properties of EGDM Networks[a]

EGDM (Vol %)	v_d (mL/g)	q_w	d_0 (g/mL)	$P\%$	V_p (mL/g)	q_v
100.0	0	1.12	1.20	0	0	1.17
90.9	0.095	1.23	1.11	7.5	0.068	1.22
80.0	0.238	1.37	0.982	18.2	0.185	1.24
71.4	0.381	1.38	0.911	24.1	0.264	1.16
66.7	0.475	1.48	0.830	30.8	0.371	1.15
60.0	0.635	1.62	0.820	31.7	0.386	1.27
54.1	0.808	1.82	0.635	47.1	0.741	1.13
50.0	0.952	1.86	0.655	45.4	0.693	1.20
47.6	1.048	2.10	0.618	48.5	0.785	1.30
44.4	1.193	2.12	0.571	52.4	0.918	1.21
40.0	1.429	2.22	0.513	57.3	1.116	1.15
33.3	1.908	2.57	0.466	61.2	1.313	1.23
20.0	3.810	4.21	0.314	73.8	2.351	1.42
11.1	7.628	7.33	0.193	83.9	4.348	1.57

[a] v_d = volume of toluene added per gram of the EGDM monomer; q_w and q_v are the equilibrium weight and volume swelling ratio of the networks in toluene, respectively; d_0 = apparent density; $P\%$ = total porosity, and V_p = pore volume of the networks.

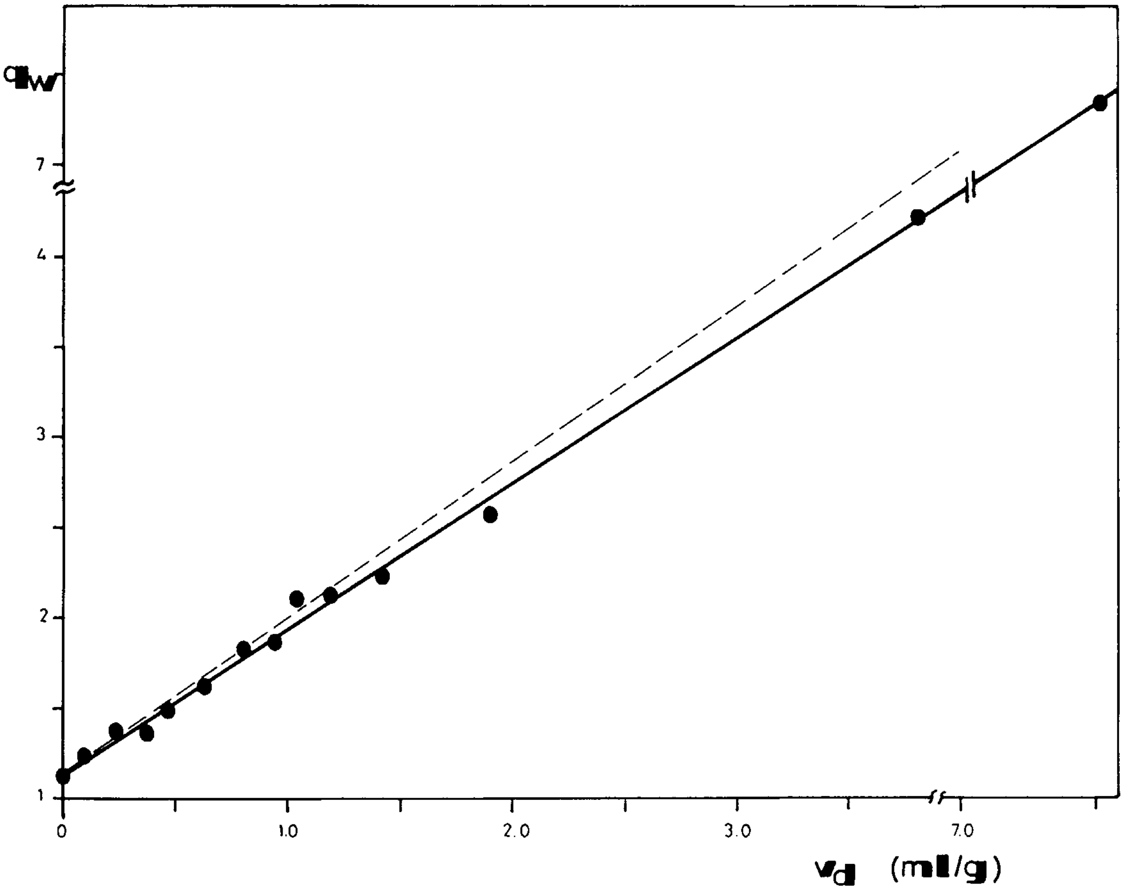


Figure 8 Dependence of the weight swelling ratio of EGDM networks in toluene, q_w, on the initial monomer dilution in terms of v_d (volume of the diluent added per gram of the monomer). The solid line is the best fit to the experimental data. The dashed line was calculated using eq. (7).

culated using eq. (7) for $q_{w,0} = 1.12$ (Table II) and $d_1 = 0.867$ g/cm^3 (density of toluene). The results show that the weight swelling ratio of EGDM networks is a linear function of the monomer dilution. The q_w vs. v_d line obtained from the experimental data is in good agreement with the theoretical line of eq. (7). The slight deviation at high dilutions ($v_d > 1.90$) may be a result of experimental error or of a loss of a small fraction of the diluent during the network formation process. A similar linear relation between q_w and v_d was also observed previously in styrene–divinylbenzene (DVB) networks having a constant DVB content.[8,13,28] Thus, eq. (7) can be used as a general equation to predict the weight swelling ratio of heterogeneous networks from their synthesis conditions.

Results of measurements of pore volume of the network samples, V_p, are shown as experimental points in Figure 9 as a function of the monomer dilution (v_d). The change in the values of V_p is at first abrupt and then slowly increases as the monomer dilution increases. At low and medium degrees of monomer dilutions, pore volume of the networks increases linearly with increasing dilution. The solid line in Figure 9 represents the best-fitting line through the experimental points between $v_d = 0$ and 1.429, given by the equation

$$V_p = 0.78 v_d \qquad (8)$$

with a correlation coefficient $r = .9898$. Deviation from linearity is observed at monomer dilutions above $v_d = 1.429$ and the rate of increase in V is decreased. All the experimental data points in Figure 9 fit the equation

$$V_p = 0.04 + 0.71 v_d - 0.02 v_d^2 \qquad (9)$$

with $r = .9982$ (solid curve).

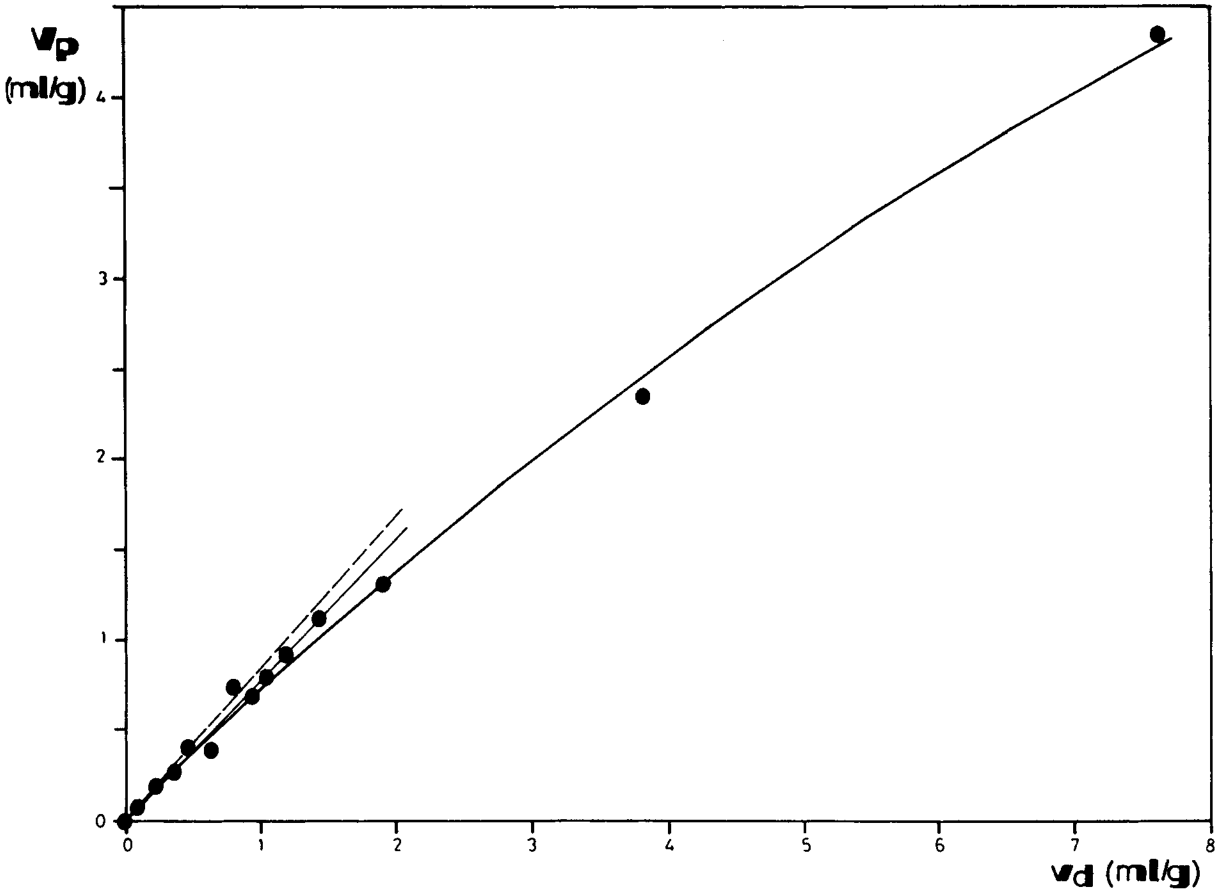


Figure 9 Dependence of the pore volume of EGDM networks, V_p, on the initial monomer dilution (v_d). The solid line is the best fit to the experimental data points between $v_d = 0$ and 1.429. The dashed line was calculated using eq. (14).

The linear $V_p - v_d$ relation and the departure from linearity at high dilutions can be explained by consideration of the porosity–swelling–dilution relations in heterogeneous networks. It is known that the swelling of heterogeneous networks is governed by two separate processes:

1. Solvation of network chains: The main driving force of this process is the changes in the free energies of mixing and elastic deformation during the expansion of the network. The extent of network solvation is determined by the cross-linking density of the network and by the interactions between solvent molecules and the network chains.[29]
2. Filling of voids (pores) by the solvent: The extent of this process is determined by the total volume of (open) pores, i.e., by the volume of diluent separated out of the network phase during the polymerization.

Since the equilibrium weight swelling ratio, q_w, includes the amount of solvent taken by the whole network (gel + pores), both of these processes are responsible for the q_w values. On the contrary, if we assume isotropic swelling, that is the volume of pores remains constant upon swelling, volume swelling of heterogeneous networks is caused by the solvation of the network chains, i.e., by the first process. Thus, the volume swelling ratio, q_v, only includes the amount of solvent taken by the gel portion of the network. Accordingly, q_v values of heterogeneous networks together with the degree of monomer dilution may give information on the distribution of the diluent between gel and diluent phases at the end of the network formation process and can be used in the calculation of pore volume of the networks.

Depending on the distribution of the diluent (or solvent) in the network structure, the networks can be classified into three groups:

1. Expanded (preswollen) networks: Expanded network structures are obtained if the diluent present during the network formation remains in the gel throughout the polymerization. Expanded networks are thus nonporous. During the removal of the diluent and drying, the expanded network collapses, but reversibly, so that on addition of a good solvent, it reexpands to its earlier state. Both the weight and volume degrees of swelling of expanded networks increase with increasing dilution due to the increasing solvation of the network chains.
2. Heterogeneous dry networks: The diluent separates totally out of the network phase during the polymerization and acts only as a pore-forming agent. The increase in the weight swelling ratio with increasing dilution is due to the increasing volume of pores, which are filled with solvent. Since the diluent exists as a separate phase during the polymerization, the effects of cyclization and change in the contents of trapped entanglements on the network structure can be neglected. Thus, the volume degree of swelling does not change with the degree of dilution.
3. Heterogeneous swollen networks: The diluent separates partially out of the network phase during the polymerization. Thus, it distributes between network and diluent phases after synthesis. A part of the diluent acts as a pore-forming agent, whereas the other part remains in the network structure and increases its volume degree of swelling.

Assuming isotropic swelling, the volume swelling ratio of the networks, q_v, can be calculated from their weight swelling ratio, q_w, and apparent density, d_0, as follows:

$$q_v = d_0\left(\frac{1}{d_2} + \frac{q_w - 1}{d_1}\right) \tag{10}$$

where d_1 and d_2 are densities of the swelling agent and the homogeneous polymer, respectively. The calculated volume swelling ratio of the networks in toluene are collected in Table II and also given in Figure 10 as experimental points plotted against the monomer dilution (v_d).

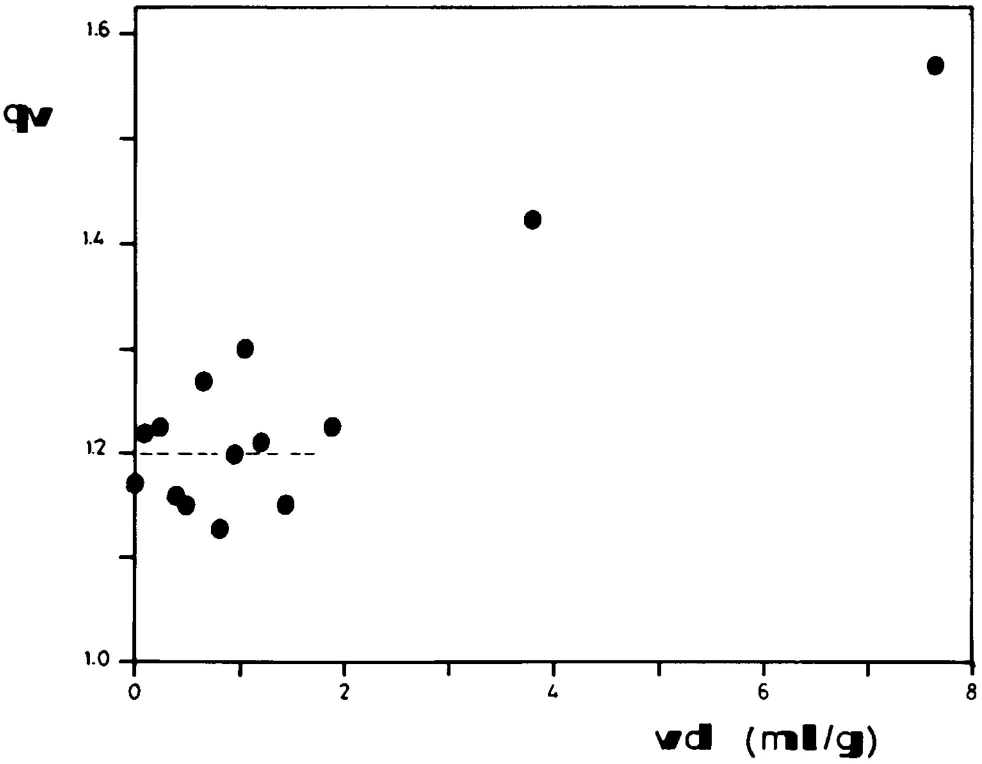


Figure 10 Dependence of the volume swelling ratio of the networks (q_v), calculated using eq. (10), on the initial monomer dilution (v_d). The dashed line illustrates the independence of q_v values on the monomer dilution between $v_d = 0$ and 1.429.

Substitution of eq. (7) into the eq. (10) leads to

$$q_v = d_0\left(\frac{q_{v,0}}{d_2} + v_d\right) \qquad (11)$$

where $q_{v,0}$ is the value q_v of the network prepared in the absence of a diluent (volume swelling ratio of homogeneous networks).

Using eqs. (2) and (11), the pore volume of the networks, V_p, can be calculated as

$$V_p = \frac{1}{q_v} v_d - \frac{1}{d_2}\left(1 - \frac{q_{v,0}}{q_v}\right) \qquad (12)$$

Equation (12) predicts the pore volume of the networks from the volume swelling ratio of heterogeneous and corresponding homogeneous copolymers and from the degree of monomer dilution. The only assumption inherent in the derivation of eq. (12) is the isotropic swelling condition of the networks.

In the case of heterogeneous dry networks, since $q_v = q_{v,0}$, the second term of eq. (12) vanishes and it reduces to the form

$$V_p = \frac{1}{q_{v,0}} v_d \qquad (13)$$

The condition of validity of eq. (13) is high cross-linking densities and low or medium diluent concentrations. Taking $q_{v,0} = 1.17$ (Table II), the pore volume of heterogeneous, dry EGDM networks can be calculated as

$$V_p = 0.85 v_d \qquad (14)$$

The dashed line in Figure 9 was calculated using eq. (14). Satisfactory agreement between the calculated $V_p - v_d$ dependence and the results from measurements [eq. (8)] is observable, indicating that all toluene separates out of the network phase during the course of the polymerization at diluent concentrations between $v_d = 0$ and 1.429. Indeed, the values q_v for these networks are almost constant and is equal to 1.20 ± 0.06 with respect to the value $q_{v,0} = 1.17$ (Fig. 10). These results also confirm the validity of isotropic swelling condition in porous networks.

At high dilutions, it is reasonable to expect that a part of the diluent remains in the gel phase after synthesis due to the good solvating character of toluene for EGDM polymers. This causes an increase in the volume swelling ratio and, according to eq. (12), a decrease in the slope of $V_p - v_d$ dependence, as was observed for diluent concentrations above $v_d = 1.429$ (Figs. 9 and 10).

CONCLUSIONS

EGDM networks prepared by free-radical polymerization in toluene as a diluent are heterogeneous, showing that a phase separation exists in the polymerization system. Both the equilibrium weight swelling ratio, q_w, and the pore volume, V_p, of the networks increase with increasing monomer dilution. Depending on the synthesis conditions, EGDM networks contain various amounts of pendant vinyl groups; only a small fraction of them is accessible to low molecular weight reactants. The accessibility of pendant vinyls was found to increase as the cross-linking density of the network decreases or as its porosity increases. The results can be explained with the formation of highly cross-linked microgels as the intermediates in the network formation processes.

Two equations were derived to predict the equilibrium weight swelling ratio and the pore volume of heterogeneous networks. These are

$$q_w = q_{w,0} + d_1 v_d$$

$$V_p = \frac{1}{q_v} v_d - \frac{1}{d_2}\left(1 - \frac{q_{v,0}}{q_v}\right)$$

Satisfactory agreement of the results of measurements with the predictions of the equations presented was observed. The equations also explain well the change of the polymer morphology depending on the synthesis conditions.

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